



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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In re Application of: :  
N. Kuzuhara et al. :  
Serial No. 10/690,697 :  
Filed: October 23, 2003 :  
For: OPTICAL COMPENSATION :  
SHEET AND LIQUID CRYSTAL :  
DISPLAY :  
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DECLARATION

Honorable Commissioner of Patents  
and Trademarks  
Washington, D.C. 20231

Sir:

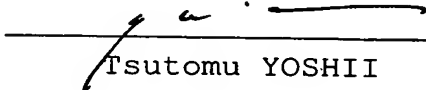
I, Tsutomu YOSHII hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 220538/2000.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with

the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

  
Tsutomu YOSHII

Dated: This 14th day of September, 2005.

**Patent Application No. 220538/2000**

**Title of the Document:** APPLICATION FOR PATENT

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<b>Title of Document:</b>	Specification	1
<b>Title of Document:</b>	Drawings	1
<b>Title of Document:</b>	Abstract	1

**Necessity of Proof** Required





[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION]

OPTICAL COMPENSATION FILM, AND POLARIZING PLATE AND  
LIQUID CRYSTAL DISPLAY EMPLOYING THE SAME

[WHAT IS CLAIMED IS:]

Claim 1. An optical compensation film comprising an optically biaxial cellulose ester film having thereon a layer, comprising a liquid crystalline compound, which is modified to an optically anisotropic layer upon fixing the orientation of said liquid crystalline compound.

Claim 2. The optical compensation film of claim 1, wherein a liquid crystalline compound is rod-shaped, and the average of the angle between the direction resulting in the maximum refractive index of said liquid crystalline compound and the surface of said cellulose ester film exceeds 0 degree but is less than 80 degrees.

Claim 3. The optical compensation film of claim 2, wherein the angle between the direction resulting in the maximum refractive index of said rod-shaped liquid crystalline compound and the surface of said cellulose ester film varies from 0 to 90 degrees.

Claim 4. The optical compensation film as claimed in one of claims 1 through 3, wherein a projection direction

within the surface of a cellulose ester film in the direction resulting in the maximum refractive index of a rod-shaped liquid crystalline compound is orthogonal to the direction resulting in the maximum refractive index of said cellulose ester film.

Claim 5. The optical compensation film as claimed in one of claims 1 through 3, wherein the projection direction within the surface of the film in the direction resulting in the maximum refractive index of a rod-shaped liquid crystalline compound is equal to the direction resulting in the maximum refractive index of said cellulose ester film.

Claim 6. The optical compensation film as claimed in one of claims 1 through 3, wherein projection direction A within the surface of the cellulose ester film which comprises at least two optically anisotropic layers A and B, in which said optically anisotropic layer A comprises rod-shaped liquid crystalline compound A, and optically anisotropic layer B comprises rod-shaped liquid crystalline compound B, and which is in the direction resulting in the maximum refractive index of said liquid crystalline compound B is orthogonal to projection direction B within the surface of the direction resulting in the maximum refractive index of said liquid crystalline compound B, and any one angle on

said projection directions A or B is equal to the direction resulting in the maximum refractive index of said cellulose ester film.

Claim 7. The optical compensation film as claimed in one of claims 1 through 6, wherein said rod-shaped liquid crystalline compound optically exhibits positive uniaxial properties and the plane retardation value of the optically anisotropic layer is in the range of from 10 to 300 nm and the retardation value in the thickness direction is in the range of 15 to 300 nm.

Claim 8. The optical compensation film as claimed in one of claims 1 through 7, wherein the retardation value within the surface of an optically biaxial cellulose ester film is in the range of from 10 to 300 nm, and the retardation value in the thickness direction is in the range of from 15 to 300 nm.

Claim 9. The optical compensation film as claimed in one of claims 1 through 8, comprising at least one orientation layer and at least one dissolving-out blocking layer between the optically biaxial cellulose film and the optically anisotropic layer.

Claim 10. The optical compensation film of claim 9, wherein said dissolving-out blocking layer comprises a water-soluble polymer.

Claim 11. The optical compensation film of claim 8 or 9, wherein said orientation layer is an optical orientation layer.

Claim 12. A polarizing plate which is prepared by adhering the optical compensating film as claimed in any one of claims 1 through 11.

Claim 13. A liquid crystal display apparatus comprising the polarizing plate as claimed in any one of claims 1 through 11.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION]

The present invention relates to an optically compensation film and a liquid crystal display.

[0002]

[BACKGROUND OF THE INVENTION]

The following three methods as described below have been proposed as an optically compensation film for obtaining a wide viewing angle of a liquid crystal display.

[0003]

(1) a method providing a discotic liquid crystalline compound, which is a negative uniaxial compound, on a support.

(2) a method providing on a support a nematic polymeric liquid crystalline compound with a positive optical anisotropy, which is subjected to hybrid orientation in which the pretilt angle of the liquid crystal molecules varies in the thickness direction.

(3) a method providing on a support two layers containing a nematic liquid crystalline compound with a positive optical anisotropy, in which the orientation direction of the layers crosses each other at approximately 90 degrees, so that an optical property approximate to a negative uniaxial optical property is obtained.

However, the above methods have the following problems.

[0004]

Method (1) shows a defect specific to a discotic liquid crystalline compound in that, in a TN mode liquid crystal display panel employing the discotic liquid crystalline compound, the displayed image appears yellowish, when viewing the panel obliquely.

[0005]

In the method (2) a temperature developing a liquid crystal is high and orientation cannot be fixed on an isotropic transparent support such as TAC (cellulose triacetate), and requires additional processing, in which a liquid crystalline compound is oriented and fixed on a first support, and transferred onto a second support such as TAC. This processing is more complex, resulting in lowering of productivity.

[0006]

There is disclosed in, for example, Japanese Patent O.P.I. Publication No. 8-15681, one example of an optically anisotropic layer employing a positive uniaxial low molecular weight liquid crystalline compound according to method (3). The example is an optically anisotropic layer comprised of four layers which consist of a first oriented layer having an orientation ability, a rod-shaped, positive uniaxial low molecular weight liquid crystalline compound layer, in which the liquid crystalline compound is oriented and fixed, provided on the first oriented layer, a second oriented layer having an orientation ability provided on the rod-shaped, positive uniaxial low molecular weight liquid crystalline compound layer, and a rod-shaped, positive uniaxial low molecular weight liquid crystalline compound

layer, in which the liquid crystalline compound is oriented and fixed, provided on the second oriented layer. In this example, a property approximate to a disc-shaped compound can be obtained, for example, by arranging the two rod-shaped, liquid crystalline compound layers so that the orientation directions in the plane of the two layers cross each other at 90 degrees.

[0007]

Accordingly, method (3) above is extremely advantageous in usage in a liquid crystal television giving priority to color reproduction, since there is no problem of yellowing occurring in the use of a discotic liquid crystalline compound.

[0008]

Although the use of the discotic liquid crystalline compound requires only one layer, however, the method requires two liquid crystalline compound layers, resulting in lowering of efficiency.

[0009]

However, the above three methods have, in common, a fundamental problem. That is, in order to obtain optical compensation ability, these methods require an optical compensation film to be provided on both sides of, for

example, a liquid crystal cell. This means that even the method for employing an optical compensation film, which is convenient for improving viewing angle, results in a cost increase. In these methods, the use of one optical compensation film destroys symmetry, and results in asymmetry of the viewing angle. For example, when the optical compensation film, the rubbing axis of which is rotated 45 degrees, is arranged, symmetry may be improved but the viewing angle property is not improved. There have been no proposals in which the use of only one optical compensation film improves the viewing angle property to the same degree as or more than two optical compensation films.

[0010]

It is therefore desired to dissolve the problems mentioned above.

[0011]

#### [PROBLEMS TO BE SOLVED BY THE INVENTION]

An objective of the present invention is to provide an optical compensation film which readily improves viewing angle characteristics of TN type LCD such as TN-TFT, that is, image contrast, coloring, and reversal phenomena of light-and-shadow, which are obliquely viewed, and further to provide a polarized plate and a liquid crystal display



apparatus with marked improvement of the viewing angle under a simple constitution, while employing said optical compensation film.

[0012]

[MEANS TO SOLVE THE PROBLEMS]

The aforementioned objective was accomplished utilizing items 1 through 13 described below.

[0013]

1. An optical compensation film comprising an optically biaxial cellulose ester film having thereon a layer, comprising a liquid crystalline compound, which is modified to an optically anisotropic layer upon fixing the orientation of said liquid crystalline compound.

[0014]

2. The optical compensation film, described in 1 above, wherein a liquid crystalline compound is rod-shaped, and the average of the angle between the direction resulting in the maximum refractive index of said liquid crystalline compound and the surface of said cellulose ester film exceeds 0 degree but is less than 80 degrees.

[0015]

3. The optical compensation film, described in 2 above, wherein the angle between the direction resulting in the

maximum refractive index of said rod-shaped liquid crystalline compound and the surface of said cellulose ester film varies from 0 to 90 degrees.

[0016]

4. The optical compensation film, described in any one of 1 through 3, wherein a projection direction within the surface of a cellulose ester film in the direction resulting in the maximum refractive index of a rod-shaped liquid crystalline compound is orthogonal to the direction resulting in the maximum refractive index of said cellulose ester film.

[0017]

5. The optical compensation film, described in any one of 1 through 3, wherein the projection direction within the surface of the film in the direction resulting in the maximum refractive index of a rod-shaped liquid crystalline compound is equal to the direction resulting in the maximum refractive index of said cellulose ester film.

[0018]

6. The optical compensation film, described in any one of 1 through 3, wherein projection direction A within the surface of the cellulose ester film which comprises at least two optically anisotropic layers A and B, in which said optically anisotropic layer A comprises rod-shaped liquid

crystalline compound A, and optically anisotropic layer B comprises rod-shaped liquid crystalline compound B, and which is in the direction resulting in the maximum refractive index of said liquid crystalline compound B is orthogonal to projection direction B within the surface of the direction resulting in the maximum refractive index of said liquid crystalline compound B, and any one angle on said projection directions A or B is equal to the direction resulting in the maximum refractive index of said cellulose ester film.

[0019]

7. The optical compensation film, described in 1 through 6 above, wherein said rod-shaped liquid crystalline compound optically exhibits positive uniaxial properties and the plane retardation value of the optically anisotropic layer is in the range of from 10 to 300 nm and the retardation value in the thickness direction is in the range of 15 to 300 nm.

[0020]

8. The optical compensation film, described in 1 through 7 above, wherein the retardation value within the surface of an optically biaxial cellulose ester film is in the range of

from 10 to 300 nm, and the retardation value in the thickness direction is in the range of from 15 to 300 nm.

[0021]

9. The optical compensation film, described in 1 through 10 above, comprising at least one orientation layer and at least one dissolving-out blocking layer between the optically biaxial cellulose film and the optically anisotropic layer.

[0022]

10. The optical compensation film, described in 11 above, wherein said dissolving-out blocking layer comprises a water-soluble polymer.

[0023]

11. The optical compensation film, described in 8 or 9 above, wherein said orientation layer is an optical orientation layer.

[0024]

12. A polarizing plate which is prepared by adhering the optical compensating film described in any one of 1 through 11 above.

[0025]

13. A liquid crystal display apparatus comprising the polarizing plate described in any one of 1 through 11 above.

[0026]

The present invention will now be detailed.

Optical compensation films according to the invention will be described.

[0027]

When conventional optical compensating film is employed, the present situation is that a commercially viable optical compensation function is obtained only by arranging said optical compensation film on both sides of said liquid crystal cell. By contrast, the inventors of the present invention discovered that to their surprise, by utilizing an optical compensation film having the constitution described in any one of claims 1 through 14, a markedly excellent optical compensation function was obtained by arranging only one optical compensation film between the liquid crystal cell and the polarizing plate.

[0028]

It was verified that the optical compensation film of the present invention exhibited excellent optical compensation functions such as high contrast when viewed from an oblique direction, and also exhibited an excellent so-called wide viewing angle, as well as no coloration in the image area, narrowing the reversal area, and the like.

[0029]

One optical compensation film of the present invention per liquid cell exhibits sufficient optical compensation function. Accordingly, when liquid crystal display apparatuses are prepared, it is possible to reduce the cost for said optical compensation film by a half compared to cases in which conventional optical compensation film is used.

[0030]

Further, commonly in the preparation of a polarizing plate, the surface treated state is different between the observer' surface side and the back surface of the liquid cell. For example, a special polarizing plate is used the surface of which is subjected to AG (antiglare) treatment and the like. In this case, a polarizing plate surface of which becomes different from the back surface. As a result, it has been essential that the optical compensation film be adhered onto each of the surfaces of said polarizing plate. Further, when problems occur in the process of adhering the optical compensation film onto the surface-treated polarizing plate, it is essential to discard said surface treated polarizing plates, at an inevitable increase in cost.

[0031]

Further, it is possible to prepare an optical compensation film employing one sheet of cellulose ester film. This results in great practical advantages that it is possible to prevent a decrease in light transmittance due to said optical compensation film by approximately half.

[0032]

The present invention makes it possible to provide an optical compensation film having a practically sufficient optical compensation function by the use of only one sheet of said film and a polarizing plate, as well as a liquid crystal display apparatus employing said optical compensation film, and more specifically, minimizes contrast variation due to the viewing angle which is specific to the twisted nematic (TN) type liquid crystal, and specifically minimizes the viewing angle dependency of the display of an active matrix type TN type liquid crystal display apparatus, specifically employed as a full color display.

[0033]

An optically biaxial cellulose ester film support associated with the present invention will now be described.

[0034]

The optical compensation film of the present invention employs an optically biaxial cellulose ester as the support. It is possible to obtain such optical characteristics by providing tension in a definite direction during the process in which cellulose ester is commonly cast. For example, it is particularly effective to carry out operations such as stretching and the like under conditions in which residual solvents still exist after casting a cellulose ester film.

[0035]

Preferably employed as cellulose ester is cellulose triacetate. Furthermore, in order to obtain optical compensation performance exceeding the specified level, it is extremely effective to employ lower fatty acid cellulose ester having specified substituents, namely an acetyl group as well as a propionyl group.

[0036]

Proffered is cellulose ester which is employed to prepare cellulose ester film associated with the present invention has an acyl group having from 2 to 4 carbon atoms as the substituent, and cellulose ester, which simultaneously satisfies the aforementioned formulas (1) and (2).

[0037]



$$(1) \quad 2.0 \leq A + B \leq 3.0, \text{ and}$$

$$(2) \quad A < 2.4$$

In the formulas, "A" represents the degree of substitution of acetyl group and "B" represents the degree of substitution of acyl group having 3 or 4 carbon atoms.

[0038]

Further, preferably employed is the cellulose ester film, which simultaneously satisfied the aforementioned formulas (3) and (4).

[0039]

$$(3) \quad 2.4 \leq A + B \leq 2.8, \text{ and}$$

$$(4) \quad 1.4 \leq A \leq 2.0$$

These acyl groups may evenly be substituted to the 2-position, the 3-position and the 6-position of glucose units, or substitution may be carried out so as to form a distribution in which, for example, the 6-position has a higher frequency, or the like.

[0040]

The degree of substitution, as described herein, refers to the percentage of the amount of so-called combined fatty acids, and the value which is calculated based on the measurement of the degree of acetylation and calculation

thereof in ASTM-D817. It is possible to determine the degree of acyl substitution, employing the ASTM-D817-96 method.

[0041]

By regulating the degree of substitution of an acetyl group and an acyl group having 3 or 4 carbon atoms in said range, it is possible to obtain a cellulose ester film support which exhibits characteristics in which the phase difference increases as the wavelength increases, and which is disposed with the desired moisture content as well as water barrier properties.

[0042]

The average degree of acetyl group substitution is particularly preferred to be less than 2.0 due to minimization of the fluctuation in phase difference during stretching.

[0043]

Further, from the viewpoint of obtaining an optical compensation film which exhibits excellent mechanical strength, the viscosity average degree of polymerization (the degree of polymerization) of the cellulose ester film, employed in the present invention, is preferably from 200 to 700, and is more preferably from 250 to 500.

[0044]

It is possible to obtain said viscosity average degree of polymerization (DP) employing the method described below.

«Measurement of Viscosity Average Degree of Polymerization (DP)»

Dissolved in 100 ml of a solvent mixture consisting of methylene chloride and ethanol (in a ratio of 9 : 1 by weight) was 0.2 g of absolutely dried cellulose ester. The falling time in second of the resultant solution was determined at 25 °C, employing an Ostwald Viscosimeter, and the degree of polymerization was obtained employing the formula described below.

[0045]

$$\eta_{rel} = T/T_s[\eta] = (\ln \eta_{rel})/CDP = [\eta]/K_m$$

wherein T is the falling time in seconds of a measured sample, T<sub>s</sub> is the falling time in seconds of the solvent, C is the concentration of cellulose ester (in g/liter), and K<sub>m</sub> = 6 × 10<sup>-4</sup>.

[0046]

From the viewpoint to more preferably obtain the desired effects to widen the viewing angle in the cellulose ester film according to the present invention, it is preferable that the relationship defined in Formula (I) be held.

[0047]

Formula (I)  $(n_x + n_y)/2 - n_z > 0$

Further, when the biaxial cellulose ester support, employed in the present invention, is optically biaxial, effects to improve the viewing angle are noted. It is possible to specify appropriate conditions utilizing retardation value  $R_t$  in the thickness direction and retardation value  $R_0$  in the plane. By controlling these values, it is possible to markedly improve the desired viewing angle widening effects. Employed as specific control methods may be a stretching method described below and the like.

[0048]

Retardation value  $R_t$  in the thickness direction, which is defined by Formula (II) described below, is preferably from 15 to 300 nm, and is more preferably from 60 to 250 nm.

[0049]

Formula (II)  $[(n_x + n_y)/2 - n_z] \times d$

wherein  $n_x$  and  $n_y$  each represent the refractive index in the x direction and the y direction in the plane of said cellulose ester film,  $n_z$  represents the refractive index in the direction of thickness, and  $d$  represents the thickness (in nm) of said film.

[0050]

Further, retardation value  $R_0$  in the plane direction is expressed by the formula described below.

$$R_0 = (n_x - n_y) \times d$$

In the formula  $d$  represents the thickness (in nm) of said film.

[0051]

In the present invention,  $R_0$  is preferably in the range of from 10 to 300 nm, and is more preferably in the range of from 40 to 150 nm.

[0052]

Said retardation values  $R_t$  and  $R_0$  are obtained as follows. Three-dimensional refractive indices,  $n_x$ ,  $n_y$ , and  $n_z$ , are determined at a wavelength of 590 nm under an ambience of 23 °C and 55 percent relative humidity employing an automatic birefringence meter KOBRA-21ADH (manufactured by Oji Keisokukiki Co., Ltd.). Said retardation values are calculated utilizing resultant  $n_x$ ,  $n_y$ , and  $n_z$ .

[0053]

The light transmittance of the optically biaxial cellulose ester film according to the present invention is preferably at least 80 percent. Further, the thickness of

the cellulose ester film support according to the present invention is preferably from 30 to 150 nm.

[0054]

Employing acid anhydrides and acid chlorides as the acylating agents, it is possible to synthesize the mixed fatty acid ester of cellulose used in the present invention. When said acylating agents are acid anhydrides, organic acids (for example, acetic acid) and methylene chloride are used as the reaction solvents. When the acylating agents are acid chlorides, basic compounds are used as the catalysts. In the most common industrial synthetic method, cellulose undergoes esterification employing mixed organic acid component, comprising organic acids (acetic acid and propionic acid) or acid anhydrides thereof (acetic anhydride and propionic anhydride) which correspond to an acetyl group and a propionyl group. The used amount of the acetylating agent and propionylating agent is regulated so that the degree of substitution of the synthesized ester falls in the range described above. The used amount of reaction solvents is preferably from 100 to 1,000 weight parts with respect to 100 weight parts of cellulose, and is more preferably from 200 to 600 weight parts. The used amount of catalysts is preferably from 0.1 to 20 weight parts with respect to 100

weight parts of cellulose, and is more preferably from 0.4 to 10 weight parts.

[0055]

The reaction temperature is preferably from 10 to 120 °C, and is more preferably from 20 to 80 °C. Further, other acylating agents (for example, a butylating agent) and etherifying agents may be employed in combination. Still further, after the completion of the acylating reaction, if desired, the degree of substitution may be regulated employing hydrolysis (saponification). After the completion of the reaction, a mixed fatty acid ester of cellulose (cellulose acetate propionate) is obtained by collecting a reaction mixture employing common methods such as precipitation, washing the resultant precipitate and subsequently drying it.

[0056]

Employed individually or in combination as the fatty acid cellulose ester of the present invention are fatty acid ester synthesized employing cotton linters and fatty acid ester synthesized from wood pulp. Cellulose ester synthesized employing cotton linters is preferably employed at a larger ratio, because it is more readily peeled from a belt or drum, and thus enhances productivity. When the

content of cellulose ester synthesized employing cotton linters is at least 60 percent, the peeling properties are markedly improved. Therefore, the content is preferably at least 60 percent, is more preferably at least 85 percent, and is most preferably 100 percent.

[0057]

The cellulose ester employed in the invention, which is acylated by acetyl group and acyl group having 3 or 4 carbon atoms, is called as mixed fatty acid ester of cellulose.

[0058]

Example of acyl group having 3 or 4 carbon atoms includes propionyl group and butyryl group. Propionyl group or n-butyryl group is preferable, and particularly propionyl group is preferable in view of mechanical strength when it is prepared in a film form and easy handling in dissolving process.

[0059]

Listed as solvents which dissolve the fatty acid cellulose ester of the present invention and form a dope may be methylene chloride, methyl acetate, ethyl acetate, amyl acetate, acetone, tetrahydrofuran, 1,3-dioxolan, 1,4-dioxolan, cyclohexanone, 2,2,2-trifluoroethanol, 2,2,3,3-



tetrafluoro-1-propanol, 1,3-difluoro-2-propanol, and the like.

[0060]

Incidentally, chlorine based solvents such as methylene chloride may be employed without causing any problem from the technical aspect. Methyl acetate, ethyl acetate, acetone, and the like, are preferable since they cause the least environmental problem. Specifically, the content of methyl acetate is preferably at least 50 percent by weight with respect to the total organic solvents. Acetone is preferably employed in an amount of 5 to 30 percent by weight with respect to the total organic solvents, together with methyl acetate, because it makes it possible to decrease the dope viscosity.

[0061]

In the present invention, containing of as little as possible chlorine based solvents means that the content of the chlorine based solvents is no more than 10 percent with respect to the total organic solvents, is more preferably no more than 5 percent, and is most preferably 0 percent.

[0062]

In addition to the organic solvents described above, alcohols having from 1 to 4 carbon atoms are preferably

incorporated into the fatty acid cellulose ester dope of the present invention in an amount of 1 to 30 percent. When alcohols are incorporated, after casting the dope onto a support, solvents start to evaporate and the web (a dope layer formed by casting a dope on a casting support is designated as the web) is gelled and the web is strengthened. Thus it is possible to more readily peel the web from the support. Further, it is possible to obtain effects which accelerate the dissolution of fatty acid cellulose ester. Listed as alcohols having from 1 to 4 carbon atoms are methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, and tert-butanol. Of these, ethanol is preferred, based on the stability of the resulting dope, its boiling point, drying properties, non-toxicity, and the like.

[0063]

The solid portion concentration in a dope is commonly, and preferably, between 10 and 40 percent. From the viewpoint of obtaining excellent flatness of a film, the viscosity of a dope is preferably controlled to be in the range of 100 to 500 poise (10 to 50 Pa·sec).

[0064]

The dope, which has been prepared as described above, is filtered employing a filter media, defoamed, and subsequently conveyed to the next process, employing a pump.

[0065]

Plasticizers, matting agents, UV absorbers, antioxidants, dyes, and the like may also be incorporated into said dope.

[0066]

Fatty acid ester cellulose, having an acetyl group as well as a propionyl group employed in the present invention, exhibits effects of a plasticizer. As a result, sufficient film properties are obtained without the addition of plasticizer, or at most addition in small amounts. However, plasticizers may be added for other purposes. For example, for the purpose to enhance the moisture resistance of film, added may be alkyl phthalyl alkyl glycolates, phosphoric acid esters, carboxylic acid esters, phthalic acid ester, fatty acid ester, citric acid ester and the like.

[0067]

Listed as alkyl phthalyl alkyl glycolates are, for example, methyl phthalyl methyl glycolate, ethyl phthalyl ethyl glycolate, propyl phthalyl propyl glycolate, butyl phthalyl butyl glycolate, octyl phthalyl octyl glycolate,

methyl phthalyl ethyl glycolate, ethyl phthalyl methyl glycolate, methyl phthalyl propyl glycolate, methyl phthalyl butyl glycolate, ethyl phthalyl butyl glycolate, butyl phthalyl methyl glycolate, butyl phthalyl ethyl glycolate, propyl phthalyl butyl glycolate, butyl phthalyl propyl glycolate, methyl phthalyl octyl glycolate, ethyl phthalyl octyl glycolate, octyl phthalyl methyl glycolate, octyl phthalyl ethyl glycolate, and the like.

[0068]

Listed as phosphoric acid esters may be, for example, triphenyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, phenyl diphenyl phosphate, octyl diphenyl phosphate, trioctyl phosphate, tributyl phosphate, and the like.

[0069]

Carboxylic acid esters include, for example, phthalic acid esters and citric acid esters. Listed as said phthalic acid esters may be dimethyl phthalate, diethyl phthalate, dimethoxyethyl phthalate, dimethyl phthalate, dioctyl phthalate, dibutyl phthalate, di-2-ethyl hexyl phthalate, and the like, while listed as said citric acid esters may be, for example, acetyl trimethyl citrate, acetyl triethyl citrate, and acetyl tributyl citrate.

[0070]

In addition, butyl oleate, methyl acetyl ricinoleate, dibutyl sebacate, triacetin, and the like are preferably employed individually or in combination. If desired, two or more types of plasticizers may be employed in combination. Phosphoric acid ester based plasticizers are preferred because when employed at a ratio of no more than 50 percent, the cellulose ester film is barely subjected to hydrolysis and exhibits excellent durability. Further, a low content of phosphoric acid based plasticizers is preferred.

Particularly preferred is the sole use of phthalic acid ester based or glycolic acid ester based plasticizers.

[0071]

Of these, methyl phthalyl methyl glycolate, ethyl phthalyl ethyl glycolate, propyl phthalyl propyl glycolate, butyl phthalyl butyl glycolate, and octyl phthalyl octyl glycolate are preferred, and particularly employed is ethyl phthalyl ethyl glycolate. Alternatively, two or more types of these alkyl phthalyl alkyl glycolates are employed in combination.

[0072]

The amount of plasticizers employed for said purpose is preferably between 1 and 30 percent with respect to the

cellulose ester, and is most preferably between 4 and 13 percent.

[0073]

These compounds may be added along with cellulose ester and solvents during preparation of a cellulose ester solution or may be added during the preparation of the solution or after said preparation.

[0074]

With the purpose to improve yellow hue of film, dyes are incorporated. Dyes are preferred which are capable of tinting to gray as seen in common photographic supports. However, being different from the photographic supports, since it is unnecessary to minimize light piping, only a small amount of dye addition may be sufficient. Specifically the content of dyes is preferably between 1 and 100 ppm with respect to the cellulose ester, and is more preferably between 2 and 50 ppm. Gray may be obtained by appropriately combining a plurality of dyes.

[0075]

Since cellulose ester film is tinted slightly yellow, blue or violet dyes are preferably employed. A plurality of dyes may be combined to obtain gray color.

[0076]

When films are not sufficiently slippery, they are subjected to blocking with each other, and occasionally, ease of handling is degraded. Matting agents such as fine inorganic particles including silicon dioxide, titanium dioxide, sintered calcium silicate, hydrated calcium silicate, aluminum silicate, magnesium silicate, crosslinked polymers, and the like are preferably incorporated into the film according to the present invention.

[0077]

Further, in order to decrease the haze of a film, fine particles such as silicon dioxide are preferably subjected to surface treatment employing organic substances. Cited as preferred organic substances for said surface treatment are halosilanes, alkoxysilanes, silazanes, siloxanes, and the like. The matting effect increases as the average particle diameter of fine particles increases, while transparency increases as said diameter decreases. Accordingly, the average primary particles diameter of fine particles is no more than 0.1  $\mu\text{m}$ , preferably between 5 and 50 nm, and more preferably between 7 and 14 nm. These fine particles usually exist in an aggregated form in the film and it is preferable to make the surface of the film roughness of 0.01 to 1.0  $\mu\text{m}$ . Listed as fine particles of silicon dioxide are Aerosil 200,

200V, 300, R972, R972V, R974, R202, R812, OX50, TT600 and the like, all of which are manufactured by Nihon Aerosil Co., ltd. Of these, preferably listed are Aerosil R972, R972V, R974, R202, R812, and the like.

[0078]

Said matting agents are preferably blended to obtain a film haze of no more than 0.6 percent, and a friction coefficient of no more than 0.5.

[0079]

The amount of matting agents, which are employed for said purpose, is preferably between 0.005 and 0.3 percent with respect to fatty acid cellulose ester.

[0080]

The optical characteristics of the optical compensation film of the present invention will now be described.

The optical compensating film of the present invention is characterized in that said film comprises an optically biaxial cellulose ester film support having thereon at least one optically anisotropic layer in which the orientation of liquid crystalline compounds are fixed. Said optically anisotropic layer may be comprised of one or more layers.

[0081]



Preferably employed as liquid crystalline compounds according to the present invention are rod-shaped liquid crystalline compounds as described later.

[0082]

In the present invention, optical compensation films are preferably employed in which the angle between the refractive index maximizing direction of rod-shaped liquid crystalline compounds incorporated into said optically anisotropic layer and the plane of said optically biaxial cellulose ester film support varies continuously or stepwise between from 0 to 90 degrees.

[0083]

The refractive index maximizing direction of the rod-shaped liquid crystalline compound, as described herein, commonly is the same as the long axis direction of the molecules which are the constitution units of said rod-shaped liquid crystalline compound. However, due to substituents of said liquid crystalline compound, the refractive index maximizing direction may not always be the same as the long axis direction of said molecule.

[0084]

Further, in the present invention, optical compensation films are preferably employed in which the projection

direction to the cellulose ester support plane of the refractive index maximizing direction of said rod-shaped liquid crystalline compound is approximately orthogonal or parallel to each other.

[0085]

Further, in the present invention, the preferably employed arrangement forms are as follows. On the cellulose ester film support, at least two layers are disposed each of which comprises rod-shaped liquid crystalline compounds. Further Optically Anisotropic Layers "A" and "B" are disposed which comprise rod-shaped liquid crystalline compounds of which orientation is fixed. In such an arrangement, refractive index maximizing direction "A" of said rod-shaped Liquid Crystalline Compound "A" incorporated into said Optically Anisotropic Layer "A" is approximately orthogonal to the projection direction on the plane of the cellulose ester film support, and refractive index maximizing direction "B" of said rod-shaped Liquid Crystalline Compound "B" incorporated into said Optically Anisotropic Layer "B" is approximately parallel to the projection direction in the plane of the cellulose ester film support.

[0086]

In the foregoing, said rod-shaped Liquid Crystalline Compound "A" and said rod-shaped Liquid Crystalline "B" may be the same or different.

[0087]

When said optically anisotropic layer, comprising said liquid crystalline compounds, is comprised one layer, an arrangement is more preferably employed in which the refractive index maximizing direction of said optically biaxial cellulose ester film support is approximately orthogonal to the projection direction on the plane of the optical compensation film in the refractive index maximizing direction of the optically biaxial cellulose ester film support.

[0088]

When said optically anisotropic layer, comprising said liquid crystalline compounds, is comprised two layers, the orientation direction of said rod-shaped liquid crystalline compounds of said two layers is preferred in which the refractive index maximizing axial directing of each rod-shaped liquid crystalline compound is approximately orthogonal. Being approximately orthogonal, as described herein, may have a certain range from 90 degrees which will result in almost no problems such as coloration due to

diffraction. However, said angle is preferably from 80 to 100 degrees, is more preferably from 85 to 95 degrees, and is most preferably 90 degrees.

[0089]

Incidentally, being orthogonal as described in the present invention, means that as described above, axes are approximately orthogonal to each other, while being the same direction means that axes directions are approximately parallel to each other. Being approximately parallel, as described herein, means that the angle between each of the axes is within  $\pm 10$  degrees, is preferably within  $\pm 3$  degrees, and is more preferably within  $\pm 1$  degree.

[0090]

Further, the refractive index maximizing axis (being not an optical axis) of said optically biaxial cellulose ester film support is located on the plane of said optical compensation film. However, the refractive index maximizing axis of said optically anisotropic layer is not always on the plane of said optical compensation film.

[0091]

Namely, when liquid crystalline compounds constituting one layer are, for example, optically positive uniaxial

liquid crystalline compounds, said refractive index maximizing axis becomes an optical axis. Said optical axis can have a constant value at an angle to the plane of said optical compensation film from 0 to 90 degrees. Said angle is preferably from 5 to 80 degrees, and is more preferably from 20 to 50 degrees.

[0092]

Further, an orientation state with respect to this thickness direction is allowed to take a so-called hybrid orientation in a continuous or stepwise varying distribution state. In the case of said hybrid orientation, are two major forms of the oblique variation of the axis.

[0093]

Namely, one case is that the angle of said axis (the direction resulting in the maximum refractive index in the refractive index ellipsoid of the rod-shaped liquid crystalline compound) is arranged so that said angle to the plane of said optical compensation film increases in the thickness direction of said optical compensation film from one surface (Surface "A") to other surface (Surface "B") of said optical compensation film, while another case is that the angle of said axis is arranged so that said angle decreases in the thickness direction of the same.

[0094]

It is possible to comprehend the constitution units of the rod-shaped liquid crystalline compounds, as described herein, as units having an optical axis. For example, they refer to their molecules. However, they are not limited to molecular units. When aggregates of a plurality of molecules have a definite optical axis, said constitution units may refer to said aggregates. Further, an increase or decrease in the angle to the optical compensation film plane means that the entire layer comprised of each layer has no optical axis. Said angle may continuously or intermittently increase or decrease in the thickness direction of said optical compensation film. Such an orientation state in the thickness direction of such an optical compensation film is occasionally called a hybrid orientation, hereunder. In this case, as described above, the entire liquid crystal layer has no optical axis. However, it is possible to determine an apparent average tilt angle of the entire layer as the aggregate of liquid crystal units having each optical axis.

[0095]

This can be defined as the angle of the plane of said optical compensation film to the direction in which the difference in refractive indexes between normal light and

abnormal light, when the optically anisotropic layer comprising said rod-shaped liquid crystalline compounds is viewed from the plane, including the lagging phase axis as the entire layer, as well as the normal line of said optical compensation film.

[0096]

The apparent average tilt angle of said liquid crystal layer comprised of said positive uniaxial liquid crystalline compounds is from 0 to 80 degrees, is more preferably from 5 to 80 degrees, and is still more preferably from 20 to 50 degrees.

[0097]

Further, it is possible to obtain the desired effects of the present invention when the optical characteristics of the support and the liquid crystal layer are reversed, namely when a biaxial liquid crystalline compound containing layer is disposed onto a positive uniaxial support. In this case, it is realized, for example, by applying optically biaxial liquid crystalline compounds onto a uniaxially stretched film. In this case, in the same manner as above, it is possible to maintain the angle of the axis in the refractive index maximizing direction to the plane of said optical compensation film at a constant value from 0 to 90

degrees. In addition, it is possible to result in a so-called hybrid orientation in a continuously or stepwise varied distribution state in said angle range.

[0098]

The liquid crystalline compound according to the invention will be explained below.

A liquid crystalline compound can be suitably used in order to form the optically anisotropic layer as described above by controlling the orientation. The liquid crystalline compound used in the invention will be explained below in detail.

[0099]

The liquid crystalline compound used in the invention may be a low molecular liquid crystalline compound or a polymer liquid crystalline compound. With respect to optical characteristics, a positive uniaxial rod-shaped liquid crystalline compound or a biaxial liquid crystalline compound is preferably used.

[0100]

In the invention the positive uniaxial anisotropic compounds (referred to also as the positive uniaxial compounds) or biaxial compounds having an optical property close to rod-shaped liquid crystalline compounds can be



treated as having optical properties of the rod-shaped liquid crystalline compounds and they may be included in the category of the rod-shaped liquid crystalline compounds.

[0101]

Herein, the term, "positive uniaxial" (optically uniaxial) means that in an anisotropic element having optical anisotropy, only two of refractive indices in three axis directions,  $n_x$ ,  $n_y$ , and  $n_z$  are equal and the two refractive indices are smaller than the remaining one, and the term, "biaxial" means that in an anisotropic element having optical anisotropy, any one of refractive indices in three axis directions,  $n_x$ ,  $n_y$ , and  $n_z$  are different from another.

[0102]

The positive uniaxial rod-shaped liquid crystalline compound in the invention may be a compound having a positive dielectric constant anisotropy or a compound having a negative dielectric constant anisotropy, but is preferably a compound having a positive dielectric constant anisotropy in view of easy controlling inclination of optical axis of each of crystal liquid molecules in the sheet thickness direction. The inclination of optical axis of the liquid crystalline compound having a positive dielectric constant

anisotropy may be controlled through making the liquid crystal itself inclined orientation by selecting orientation layer.

[0103]

Dielectric constant anisotropy ( $\Delta\epsilon$ ) of the rod-shaped liquid crystalline compound is represented by the difference  $\Delta\epsilon$  ( $\Delta\epsilon = \epsilon_{//} - \epsilon_{\perp} \neq 0$ ) between dielectric constant ( $\epsilon_{//}$ ) in a state in which the major axis of the molecule is oriented in parallel with the electric field direction and dielectric constant ( $\epsilon_{\perp}$ ) in a state in which the minor axis of the molecule is oriented in parallel with the electric field direction. Dielectric constant anisotropy ( $\Delta\epsilon$ ) has an influence on anisotropic property of refractive index of light transmitting liquid crystal molecules. The relationship between the both is represented by the following formula:

$$\Delta\epsilon = (n_{//})^2 - (n_{\perp})^2$$

wherein  $\Delta n = n_{//} - n_{\perp} = n_e - n_o$ , wherein  $n_e$  represents an extraordinary light refractive index, and  $n_o$  represents an ordinary light refractive index,  $n_{//}$  represents an refractive index to light in the orientation vector direction of liquid crystal molecules, and  $n_{\perp}$  represents an

refractive index to light in the direction perpendicular to the orientation vector of liquid crystal molecules.

[0104]

Herein,  $\Delta\epsilon$  or  $\Delta n$  is a positive value in the liquid crystalline compound used for driving an ordinary TN liquid crystal cell.

[0105]

In the low molecular weight liquid crystalline compound the whole molecule determines the optically anisotropic property (typically, refractive index anisotropy) of the liquid crystalline compound. A polymer liquid crystalline compound is divided into two kinds, and the one is a main chain type polymer liquid crystalline compound and the other a side chain type polymer liquid crystalline compound. In the both type polymer liquid crystalline compounds, a structure containing a mesogenic group determines the optically anisotropic property in a similar manner as in the low molecular weight compound.

[0106]

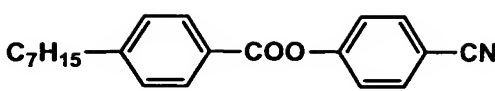
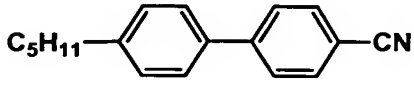
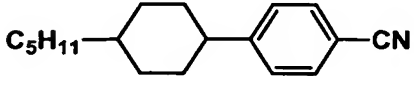
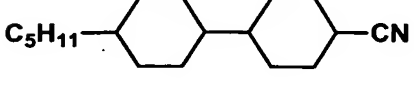
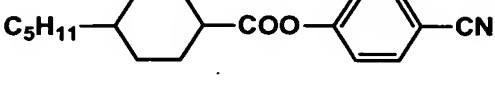
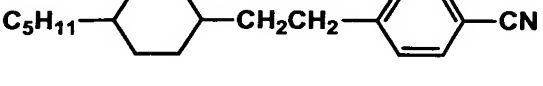
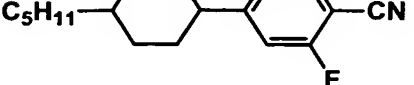
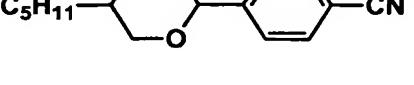
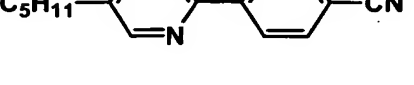
The mesogenic group (or a mesogenic unit) as described above refers to a part necessary for developing a liquid crystal property in a liquid crystalline compound, and the mesogenic group ordinarily comprises a core group being a

rigid part, a spacer group being a flexible part, and an end group positioned at the molecular end. However, the mesogenic group does not require all of the above three groups as long as a liquid crystalline compound has a group developing a liquid crystal property.

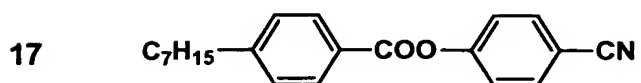
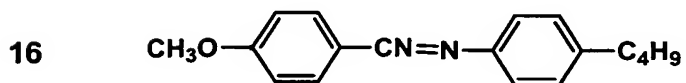
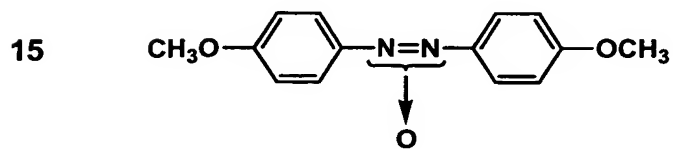
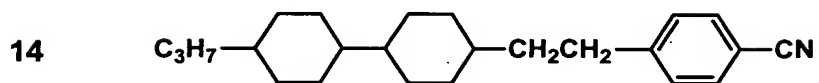
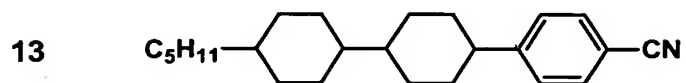
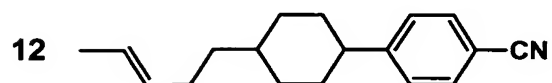
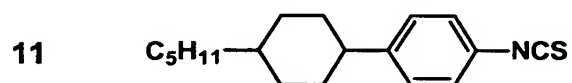
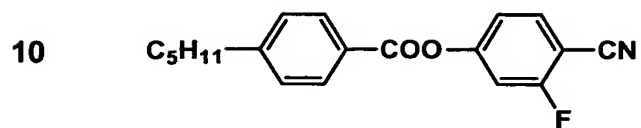
[0107]

Examples of the positive uniaxial liquid crystalline compounds will be shown below, but they are not limited thereto.

[0108]

- 1  $\text{C}_7\text{H}_{15}$ -
- 2  $\text{C}_5\text{H}_{11}$ -
- 3  $\text{C}_5\text{H}_{11}$ -
- 4  $\text{C}_5\text{H}_{11}$ -
- 5  $\text{C}_5\text{H}_{11}$ -
- 6  $\text{C}_5\text{H}_{11}$ -
- 7  $\text{C}_5\text{H}_{11}$ -
- 8  $\text{C}_5\text{H}_{11}$ -
- 9  $\text{C}_5\text{H}_{11}$ -

[0109]



[0110]

- 18 CCCCC1CCCCC1c2ccc(CCC)cc2
- 19 CCCCC1CCCCC1c2ccc(OCC)cc2
- 20 CCCCC1CCCCC1CCc2ccc(OCC)cc2
- 21 CCCCC1CCCCC1C(=O)Oc2ccc(OCC)cc2
- 22 CCCCC1CCCCC1C2CCCCC2CC
- 23 CCCCC1=CC=CC=C1C#Cc2ccc(OCC)cc2
- 24 CCCCCOc1ccc(cc1)-c2nc(CCC)ccn2
- 25 CCCCC1CCCCC1C2CCCCC2c3ccc(CCC)cc3
- 26 CCCCC1CCCCC1c2ccc(cc2)-c3ccc(CCC)cc3

[0111]

In addition to the above exemplified compounds, compounds described in "Ekisho no Kagaku: quarterly publication, Kagaku Sosetsu No. 22 (1994), p. 42, 44 edited by Nihon Kagakukai" (Gakkai Shuppan center) can be used. The above described rod-shaped liquid crystalline compounds having a positive uniaxiality can be suitably used as ordinary rod-shaped nematic liquid crystalline compounds used in TN cells.

[0112]

Compounds developing a nematic liquid crystal phase are preferably used as the rod-shaped liquid crystalline compounds in the invention.

[0113]

The biaxial liquid crystalline compounds include compounds described in Yukigoseikagaku, Vol. 49, No. 5 (1991), p. 124-143, compounds described in D.W. Bruce et al., AN EU-SPONSORED' OXFORD WORKSHOP ON BIAxIAL NEMATICS' (St Benet's Hall, University of Oxford 20-22 December, 1996), p. 157-293, compounds described in S. Chandrasekhar et al., A Thermotropic Biaxial Nematic Liquid Crystal, Mol. Cryst. Liq. Cryst., 1988, Vol. 165, pp. 123-130, and compounds described in D. Demus, J. Goodby et al., Handbook



of Liquid Crystals, Vol. 2B, Low Molecular Weight Liquid Crystals II, pp. 933-943, published by WILEY VCH Co.

[0114]

The liquid crystal polymers in the invention are not specifically limited, but are preferably ones having a positive or negative specific double refractive index, which are detailed in "LIQUID CRYSTALS, 1989, Vol. 5, No. 1, pp. 159-170".

[0115]

The polymer liquid crystalline compounds in the invention are divided into two kinds of polymer liquid crystalline compounds having a mesogenic group, one is a polymer having a mesogenic group in the main chain and the other a polymer having a mesogenic group in the side chain. The polymer liquid crystalline compounds in the invention are also divided into two kinds of thermotropic and liotropic polymer liquid crystalline compounds.

[0116]

The liquid crystal polymers in the invention are not specifically limited, but are preferably ones forming a nematic liquid crystal. The polymer having a mesogenic group in the side chain is preferable in orientation property, and a thermotropic liquid crystal polymer is preferable in

orientation fixation. The main chain used in the above side chain type liquid crystal polymers is preferably that of a vinyl type polymer, polysiloxane, polypeptide, polyphosphazene, polyethylene imine, and cellulose.

[0117]

Compounds having double refraction property but not having liquid crystalline property can be employed in place of liquid crystalline compounds in the invention. The transmittance of anisotropic layer in the range of visible light is preferably 80 % or more. It is possible to give the same optical property to compounds having no liquid crystallinity and having polarity group such as cyano, nitro group or halogen by subjecting pouring process.

[0118]

The cellulose ester film support according to the invention preferably has a function to cut off ultraviolet rays since the support is installed in a liquid crystal display which may be sometimes employed outdoor. UV absorbers are preferably incorporated into the cellulose ester film of the present invention.

[0119]

Preferably employed are UV absorbers which are excellent in absorbing ultraviolet radiation having a wavelength of

less than 370 nm to minimize degradation of the liquid crystal and absorb as little as possible visible light of wavelengths of more than 400 nm. In the present invention, the transmittance at a wavelength of 370 nm is particularly to be not more than 10 percent. The amount of the UV absorber is preferably 0.5 to 5 percent, and is more preferably 0.6 to 2.0 percent by weight with reference to the fatty acid cellulose ester.

[0120]

The UV absorber employed herewith preferably has no absorption within the visible light range, and, the example includes benzotriazole based compounds, benzophenone based compounds, salicylic acid ester based compounds, and the like.

[0121]

Examples include, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)benzotriazole, 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-n-octoxybenzophenone, 4-dodecyloxy-2-hydroxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-

dimethoxybenzophenone, phenyl salicylate and methyl salicylate.

[0122]

In the present invention, at least one of these UV absorbers is preferably employed, and more than two different UV absorbers may be incorporated in combination.

[0123]

Methods for adding UV absorbers are those in which UV absorbers are dissolved in organic solvents such as alcohol, methylene chloride, dioxolan, and the like, and then added to an organic solvent solution (hereinafter simply referred to as dope) of cellulose ester, or UV absorbers may be directly added to said dope. Inorganic powders, which are insoluble in organic said solvents are dispersed into organic solvents and cellulose ester employing a dissolver or a sand mill, and are then added to said dope.

[0124]

The employed amount of UV absorbers in the present invention is commonly between 0.1 and 2.5 percent by weight with respect to the weight of cellulose ester, is preferably between 0.5 and 2.0 weight percent by weight, and is more preferably between 0.8 and 2.0 percent by weight. An amount

of UV absorbers, exceeding 2.5 percent by weight, is not preferred due to the tendency of a decrease in transparency.

[0125]

In order to enhance the heat resistance of a film, hindered phenol based compounds are preferably employed. The added amount of these compounds is preferably between 1 ppm and 1.0 percent by weight with respect to the cellulose ester, and is more preferably between 10 and 1,000 ppm.

[0126]

Further, in addition to these compounds, heat stabilizers such as alkali earth metal salts comprised of calcium, magnesium, and the like, may also be added.

[0127]

In addition to the aforementioned compounds, further, added may be antistatic agents, flame retarders, lubricants, oils, and the like.

Foreign matter particles which generate disordered reflection light will deteriorate characteristics since the cellulose film support of the invention is employed between polarization plates. In view of this, abnormal luminescent spots become problematic.

[0128]

The luminescent spots, which are observed at a polarized light cross Nicol state, mean those which are observed in such a manner that two polarizing plates are arranged at a right angle (cross Nicol) state and said cellulose film is placed between them. Such luminescent spots at said polarized light cross Nicol state are observed only as luminescent spots caused by penetrating light from opposite side under light shielded conditions. Thus it is possible to readily identify the size as well as the number thereof.

[0129]

The number of luminescent spots having a size of 5 to 50  $\mu\text{m}$  per 250  $\text{mm}^2$ , which are observed under a polarized light cross Nicol state, is preferably not more than 200, and the number of luminescent spots having a size of at least 50  $\mu\text{m}$  is preferably 0. The number of luminescent spots having a size of 5 to 50  $\mu\text{m}$  is more preferably not more than 100, and is further more preferably not more than 50. Too many numbers of the luminescent spots affect material disadvantage on the image of a liquid crystal display.

[0130]

Preparation method of a cellulose ester film support is described.

[0131]

Preferable method for the preparation of the cellulose ester film support is solvent casting film forming method, in which dope liquid is cast on a substrate to form a film, and the film is peeled off the substrate, and after that the film is subjected to drying during conveying in the drying zone with tension. The solvent casting film forming method is described below.

[0132]

(1) Dissolution Process: The dissolution process is one in which cellulose ester flakes are dissolved, while stirring, in organic solvents mainly comprised of good solvents for said flakes, employing a dissolution vessel, and thereby a cellulose ester solution (hereinafter referred to as a dope) is prepared. In order to carry out said dissolution, there are various methods such as a method in which dissolution is carried out at a normal atmospheric pressure, a method in which dissolution is carried out at a temperature lower than the boiling point of the primary solvent, a method in which dissolution is carried out at a temperature higher than the boiling point of the main solvent under an increase of pressure, a cooling dissolution method in which dissolution is carried out at a lowering temperature, as described in

J.M.G. Cowie et al., Makromol. hem., volume 143, page 105 (1971), and Japanese Patent Publication Open to Public Inspection Nos. 9-95544 and 9-95557, and others, a method in which dissolution is carried out at a high pressure, and the like. The resultant dope is filtered employing filter materials, is then defoamed, and is subsequently pumped to the next process.

[0133]

(2) Casting process: a process in which a dope is conveyed to a pressure die through a pressure type metering gear pump, and at the casting site, said dope is cast from said pressure die onto a support for casting (hereinafter occasionally referred to as a support) which is an infinitely moving endless metal belt or a rotating metal drum. The surface of the support for casting is specular. Listed as other casting methods are a doctor blade method in which the thickness of the dope layer is regulated employing a blade, and also a reverse roll coater method in which regulation is carried out employing a roll which rotates in the reverse direction. Said pressure die is preferred in which the slit shape at the mouth piece portion can be regulated and the film thickness is readily regulated to be uniform. The pressure die includes a coat hanger die, a "T"



die, and the like, and any of these may preferably be employed. In order to increase the casting speed, at least two pressure dies may be provided and at least two layers may be simultaneously cast while dividing the dope.

[0134]

(3) Solvent evaporation process: a process in which a web is heated on the support for casting and solvents are thereby evaporated. In order to evaporate solvents, methods include one in which air is blown from the web side, and/or a method in which heating is carried out from the reverse surface of the support employing liquid, and another in which heating is carried out from the surface as well as the reverse surface employing heat radiation. Of these, the reverse surface liquid heating method is preferred due to high drying efficiency. Further, these methods are preferably combined.

[0135]

(4) Peeling process: a process in which a web, which has been subjected to evaporation of solvents on the support, is peeled at the peeling site. The peeled web is conveyed to the subsequent process. When the residual solvent amount (refer to the formula described below) is too excessive, it may be difficult to peel the web. On the contrary, when

peeling is carried out after fully drying the web on the support, a part of the web may peel prior to the peeling site.

[0136]

Listed as a method to increase the casting speed is a gel casting method (in which peeling can be carried out even though the amount of residual solvents is relatively great and high casting speed is obtained). Said gel casting methods include a method in which poor solvents with respect to the cellulose ester are added to a dope and gelling is carried out after casting said dope, and also a method in which gelling is carried out by decreasing the temperature of the support, and the like. Further, also included is a method in which metal salts are added to the dope. By strengthening the web through gelling the dope on the support, it is possible to carry out earlier peeling and to increase the casting speed. When peeling is carried out at the time when the residual solvent amount is still relatively great, the web may be too soft. Thus during peeling, the flatness of the web tends to be degraded, and wrinkles and longitudinal streaks tend to be formed. Accordingly, the residual solvent amount is determined so that productivity and quality are balanced.

[0137]

(5) Drying process: a process which dries a web employing a drying apparatus in which said web is alternatively passed through staggered rolls and/or a tenter apparatus in which said web is conveyed while the web width is maintained by holding both web edges employing pins or clips. A common drying method is one in which both surfaces of the web are subjected to hot air flow. Instead of air, employed is a method in which heating is carried out employing microwaves. Too rapid drying tends to degrade the flatness of the finished film. High temperature drying is preferably carried out when the residual solvent amount is no more than 8 percent. During the entire drying process, drying temperatures are commonly between 40 and 250 °C, and are preferably between 70 and 180 °C. Drying temperature, drying air volume, and drying time vary depending on employed solvents. Thus drying conditions may be suitably selected depending on types of employed solvents and their combination.

[0138]

In the drying process, the web tends to shrink in the width direction due to the evaporation of solvents. When

rapid drying is carried out at a relatively high temperature, shrinkage increases further. Drying is preferably carried out while minimizing the resulting shrinkage so that the finished film exhibits excellent flatness. From this viewpoint, a drying method (a tenter method), as shown, for example, in Japanese Patent Publication Open to Public Inspection No. 62-46625, is preferred in which the entire or a part of the drying process is carried out while holding both edges of the web in the width direction employing clips.

[0139]

(6) Winding process: a process in which after decreasing the residual solvent amount to no more than 2 percent, the resulting web is wound. By decreasing the residual solvent amount to no more than 0.4 percent, it is possible to obtain a film having excellent dimensional stability. Employed as winding methods may be those which are commonly employed. Said methods include a constant torque method, a constant tension method, a taper tension method, an inner stress constant program tension control method, and the like. Any of these may be selected and employed.

[0140]

The layer thickness of a fatty acid cellulose ester film is preferably controlled so as to obtain the desired thickness while controlling the dope concentration, the pumping liquid volume, the slit distance of the die mouth ring, the extrusion pressure of the die, and the speed of a casting support. Further, as a means to make the layer thickness uniform, it is preferable that by employing a layer thickness detecting means, programmed feedback information is subjected to feedback to each of said devices so that the layer thickness is controlled.

[0141]

In the processes immediately after casting to drying employing a solution casting method, air may be employed as an atmosphere in the drying apparatus. However, inert gasses as nitrogen gas, carbon dioxide gas, and the like may be employed in said drying apparatus. Naturally, attention should always be paid so that the concentration of evaporated solvents in the drying atmosphere does not exceed the explosion limit.

[0142]

In order to obtain the orientation exhibiting optically biaxial characteristics (showing the relationship of  $N_x > N_y > N_z$ ), it is possible to employ any feasible method to

prepare the cellulose ester support having optical biaxially characteristics, according to the present invention. As one of the most effective methods, it is possible to accept a stretching method.

[0143]

As described below, during production, it is possible to stretch the optical compensation film of the present without utilizing a relatively high temperature. When said method is not utilized, it is possible to carry out stretching at a relatively high temperature. In the case of high temperature stretching, stretching is carried out at a temperature higher than the glass transition temperature of said cellulose ester. However, plasticizers as described above result in a decrease in their effects and occasionally, sufficient stretching properties are not obtained. As a result, plasticizers, which can provide sufficient stretching properties even at a high temperature, have been needed. As such plasticizers, it was discovered that it was possible to efficiently employ non-volatile plasticizers. Non-volatile plasticizers, as described herein, refer to compounds which have a markedly low vapor pressure of no more than 1,330 Pa at 200 °C as well as low volatility. Said vapor pressure is more preferably no more than 665 Pa, and

is still more preferably to be no more than 133 Pa. For instance, arylenebis(diarylphosphate) ester is preferred. Other than this, tricresyl phosphate (38.6 Pa at 200 °C) and trimellitic acid tris(2-ethylhexyl) (66.5 Pa at 200 °C), and the like are also preferably employed. Further, non-volatile phosphate esters described in Japanese Patent Application Open to Public Inspection under PCT Application No. 6-501040 are preferably employed. In addition, preferably employed as plasticizers may be those having a high molecular weight such as polymers and oligomers such as polyester, acrylic resins, polyvinyl acetate containing polymers, and the like. In this case, the content of plasticizers is preferably from 0.1 to 30 percent by weight with respect to the cellulose ester, and is most preferably from 0.5 to 15 percent by weight. By employing such plasticizers, it is possible to enhance the stretching properties of cellulose ester at a relatively high temperature, and specifically to produce at high productivity cellulose ester film supports exhibiting excellent film surface quality as well as flatness.

[0144]

Preferably employed as one example of said methods, which provide optically biaxial properties with the

cellulose ester film support according to the present invention, is a method, in which, as previously described, a stretching operation is carried out under the state in which solvents are still incorporated. Said stretching method will now be described.

[0145]

In the production of the cellulose ester film support associated with the optical compensation film of the present invention, a cellulose ester-dissolved dope is cast onto a casting support. Subsequently, it is preferable that a web (a film), peeled from said casting support, is stretched in at least one direction by a factor of 0.5 to 4.0 while a residual solvent amount in said web is in the range of from 10 to 100 percent by weight.

[0146]

Incidentally, said residual solvent amount is expressed by the formula described below.

$$\text{Residual solvent amount (in percent by weight)} = \{(M - N)/N\} \times 100$$

wherein M is the weight of the web at an optional time, and N is the weight of the web which is dried at 110 °C for 3 hours since said optional time.



[0147]

When the residual solvent amount in the web is excessively large, stretching effects are not obtained. On the other hand, when the residual solvent amount is excessively small, stretching becomes markedly difficult, and the web is occasionally broken. The residual solvent amount in the web is more preferably in the range of from 10 to 50 percent by weight, and is most preferably in the range of from 20 to 40 percent by weight. Further, when the stretching factor is excessively small, it is difficult to obtain the sufficient phase difference, while when the stretching factor is excessively large, stretching becomes difficult and the web is occasionally broken. The stretching factor is more preferably in the range of 1.0 to 3.5.

[0148]

It is possible to stretch a film, which is solution-cast employing cellulose ester according to the present invention, without heating to a relatively high temperature, if the residual solvent amount is in the specified range. When stretching and drying are carried out at the same time, the process is preferably shortened. However, when the temperature of the web is excessively high, plasticizers

volatile. Accordingly, the temperature is preferably from 15 °C (room temperature) to 160 °C.

[0149]

Further, biaxial stretching, in which the stretching directions are orthogonal to each other, is an effective method so that film refractive indexes  $N_x$ ,  $N_y$ , and  $N_z$  are within the range of the present invention. For example, in the case of stretching a film in the casting direction, when the contraction in the width direction is too large,  $N_z$  becomes too large. In this case, it is possible to decrease  $N_z$  by minimizing the contraction in the width direction or carrying out stretching in the width direction. In the case of stretching in the width direction, the refractive index occasionally results in non-uniform distribution across the width. Said non-uniform distribution of the refractive index occurs when a tenter method is utilized. This phenomenon occurs in such a manner that stretching in the width direction results in a contraction force in the central area of the stretched film while the film edges are fixed. This phenomenon is assumed to be the same as the so-called Boing phenomenon. Even in this case, it is possible to minimize the Boing phenomenon by carrying out stretching in the

casting direction and to improve the non-uniform phase difference distribution across the width.

[0150]

Further, by carrying out biaxial stretching in which the stretching directions are orthogonal to each other, it is possible to decrease variations of thickness of the stretched film. When the thickness variation of the cellulose ester film support is excessively large, non-uniform phase difference occurs, which results in problems such as coloration and the like, when used as an optical compensation film. The thickness variation of said cellulose ester film support is preferably in the range of  $\pm 3$  percent, and is more preferably in the range of  $\pm 1$  percent. In order to achieve objectives as above, the method in which biaxial stretching is effective in which stretching directions are orthogonal to each other. The biaxial stretching factors, in which stretching directions are orthogonal to each other, are preferably from 0.8 to 4.0, and from 0.4 to 1.2, respectively.

[0151]

Methods to stretch the web are not particularly limited. Methods include, for example a method in which a plurality

of rolls rotate at different circumferential speed, and stretching in the longitudinal direction is carried out utilizing said different circumferential speed during the rotation of rolls; a method in which both edges of the web are secured employing clips or pins, and stretching in the longitudinal direction is carried out by increasing the distance between clips or pins in the advancing direction; a method in which lateral stretching is carried out by increasing the distance between said clips or pins in the lateral direction, a method in which longitudinal stretching and lateral stretching are simultaneously carried out by increasing the distance between said clips or pins in the longitudinal direction as well as in the lateral direction; and the like. Naturally, these methods may be employed in combination. Further, in the case of the so-called tenter method, it is preferable to drive a clip portion employing a linear drive system so as to make it possible to carry out smooth stretching and to minimize danger such as film breakage, and the like.

[0152]

The film obtained as above comprises residual solvents preferably in an amount of no more than 2 percent by weight in the finished film, and more preferably in an amount of no

more than 0.4 percent by weight so as to obtain a film with excellent dimensional stability.

[0153]

The oriented layer (orientation layer) in the invention will be explained below.

The oriented layer is generally provided on a transparent support or a subbing layer. The oriented layer controls an orientation direction of a liquid crystalline compound layer provided on it. This gives an orientation inclined to an optical compensation film. The oriented layer may any layer as long as it gives an orientation property to an optically anisotropic layer. The preferred example of the oriented layer is a rubbing layer containing an organic compound (preferably a polymer), an inorganic compound oblique evaporation layer, a layer having a microgroove, a multi-layered film (LB film) of  $\omega$ -tricosanoic acid, dioctadecylmethylammonium chloride or methyl stearate, which is formed according to a Langmuir-Projet method, and a layer having a dielectrics oriented by application of an electric or magnetic field.

[0154]

The organic compounds used for forming an oriented layer include polymers such as polymethyl methacrylate, acrylic

acid-methacrylic acid copolymer, styrene-maleimide copolymer, polyvinyl alcohol, poly(N-methylolacrylamide), styrene-vinyl toluene copolymer, chlorosulfonated polyethylene, nitrocellulose, polyvinyl chloride, chlorinated polyolefin, polyester, polyimide, vinyl acetate-vinyl chloride copolymer, ethylene-vinyl acetate copolymer, carboxymethylcellulose, polyethylene, polypropylene, and polycarbonate, and compounds such as silane coupling agents. The preferred polymers are polyimide, polystyrene, a polymer of styrene derivatives, gelatin, polyvinyl alcohol, or an alkyl modified polyvinyl alcohol (modified with preferably an alkyl having a carbon atom number of 6 or more). The oriented layer obtained by subjecting the above described polymer layer to orientation treatment can orient a liquid crystalline compound obliquely.

[0155]

Of the above described compounds, an alkyl modified polyvinyl alcohol is especially preferable. The alkyl modified polyvinyl alcohol is superior in uniformly orienting a liquid crystalline compound. This is considered to be due to a strong interaction between the alkyl chain of the liquid crystalline compound and the alkyl chain of the alkyl modified polyvinyl alcohol on the surface of the

oriented layer. The alkyl in the alkyl modified polyvinyl alcohol has a carbon atom number of more preferably 6 to 14. It is preferable that the alkyl is bonded to polyvinyl alcohol through a linkage, -S-,  $-(CH_3)C(CN)-$ , or  $-(C_2H_5)N-CS-S-$ . The alkyl modified polyvinyl alcohol is a polyvinyl alcohol having alkyl in the molecular end, and preferably has a saponification degree of 80% or more and a polymerization degree of 200 or more. The polyvinyl alcohols described above having alkyl in the side chain include products such as MP 103, MP 203, and R 1130 manufactured by Kuraray Co., Ltd.

[0156]

A polyimide layer (preferably polyimide having fluorine atoms), which is widely employed as an LCD oriented layer, is preferred as the organic oriented layer. It is possible to obtain said layer by coating, onto a transparent support, polyamic acid (for example, LQ/LX Series manufactured by Hitachi Kasei Co., Ltd., and SE Series manufactured by Nissan Kagaku Co., Ltd), heating the coated layer at 100 to 300° C for 0.5 to 1 hour, and then rubbing the resultant heated layer. The oriented layer in the invention is preferably a hardened layer obtained by hardening a layer containing a polymer, in which a reactive group is

incorporated to the above described polymer, or a mixture of the above described polymer and an isocyanate compound or an epoxy compound.

[0157]

The above described rubbing treatment may be carried out utilizing a treatment method which is widely employed as an LCD liquid crystal orientation process. That is, it is possible to employ a method in which orientation is obtained by rubbing the surface of a layer to be oriented in a definite direction, employing paper, gauze, felt, rubber, nylon, polyester fiber, and the like. Generally, the surface of the layer to be oriented is rubbed several times, employing a cloth prepared by uniformly planted fiber having a uniform length and diameter, whereby the rubbing treatment is suitably carried out.

[0158]

The evaporation substance for the inorganic oblique evaporation film include representatively  $\text{SiO}_2$ , and further metal oxides such as  $\text{TiO}_2$  and  $\text{ZnO}_2$ , fluorides such as  $\text{MgF}_2$ , and metals such as Au and Al. Metal oxides having a high dielectric constant can be used as the oblique evaporation compounds, and are not limited to the above metal oxides. An inorganic oblique evaporation film can be formed employing a



vacuum evaporation device. The inorganic oblique evaporation film can be formed by vacuum evaporating inorganic compounds on the fixed support or continuously vacuum evaporating inorganic compounds on the moving web support.

[0159]

The oriented layer employed in the invention may be any combination of the above described, and is not specifically limited, but an appropriate combination of the oriented layers and liquid crystalline compounds can provide an angle (a tilt angle) inclined to a base plane with respect to the sheet thickness direction, as described later.

[0160]

As another method for orienting liquid crystalline compounds, there is a method employing an electric field or a magnetic field. As the method for orienting liquid crystalline compounds obliquely in the invention, a magnetic field is preferably used. When a solution containing a liquid crystal molecule dispersed in a polymer matrix is coated on a support, and a magnetic field is applied to the coated at an angle to the direction perpendicular to the support plane, the liquid crystal molecule is oriented in the direction. In this case, the intensity of the magnetic field is preferably 500 G or more, but a liquid crystalline

compound with a low intrinsic viscosity can be oriented at not more than 500 G or less.

[0161]

As the rubbing methods, there are a mask rubbing method rubbing with a mask having a definite shape while moving (K. Takatori et al., "A Complementary T LCD with Wide-Viewing Angle Grayscale", Japa Display' 92, pp 591) and a coating method coating plural compounds for orientation (T. Kamada et al., Wide-Viewing Angle Full-Color TFT LCDs", Japa Display' 92, pp 886). The mask rubbing method and the method of coating plural compounds comprise complex processes.

[0162]

Further, these methods, when an oriented layer is formed, change inclined angle (so-called, a pretilt angle) of the liquid crystalline compounds used, and only form two symmetric pretilt angles. Therefore, the orientation direction is only single, and improvement of viewing angle is limited to a specific direction.

[0163]

Other methods controlling liquid crystal orientation than the rubbing method includes inclination evaporation method employing inorganic oblique evaporation film (Japanese Patent O.P.I. Publication No. 56-66826). Further

there are proposed a photolithographic method for forming grating protrusions and concaves on the surface of the orientation film according to photolithography (Japanese Patent O.P.I. Publication No. 60-60624), a LB film method for orienting a polymer chain on upper direction in providing a multi-layer on a support (Japanese Patent O.P.I. Publication No. 62-195622), an ion irradiation method for irradiating ion obliquely (Japanese Patent O.P.I. Publication No. 3-83017), a high speed liquid jetting method for jetting liquid with high speed obliquely (Japanese Patent O.P.I. Publication No. 63-96631), an ice blasting method jetting ice obliquely (Japanese Patent O.P.I. Publication No. 63-96630), an excimer laser method for forming periodical stripes by irradiating an excimer laser to a polymer surface (Japanese Patent O.P.I. Publication No. 2-196219), an electron beam scanning method for forming fine protrusions and concaves by scanning a thermoplastic compound with an electron beam (Japanese Patent O.P.I. Publication No. 4-97130), a centrifugal method for orienting a polymer chain of a coated layer by centrifugal force (Japanese Patent O.P.I. Publication No. 63-21381), a stamping method for transferring orientation by laminating a layer oriented in advance onto another base by means of

pressure (Japanese Patent O.P.I. Publication No. 6-43457), a Y. Toko et al. random orientation method for twisting orientation by adding a chiral agent (J. Appl. Phys. A74 (3), p. 2071 (1993)), and a Hasegawa et al. photo decomposition method for photo-decomposing a polyimide film employing a polarized ultraviolet light (Ekisho Toronkai Yokoshu, p. 232, (Number 2G604) (1994)).

[0164]

Orientation of the optical compensation film of the invention shows a hybrid orientation or changes its inclined degree due to a surface energy of the plane which a liquid crystal layer contacts (for example, a support plane or atmospheric air) or kind of liquid crystalline compounds mixed, which can control the orientation.

[0165]

For example, an inclined angle of the above described rod-shaped compounds on the support side can be generally adjusted by selecting liquid crystalline compounds used in the invention or compounds used in an oriented layer, or selecting rubbing treatment methods. An inclined angle of the liquid crystalline compounds on the obverse side (contacting atmospheric air) can be generally adjusted by selecting liquid crystalline compounds used in the invention

or another compound (such as a plasticizer, a surfactant, a polymerizable monomer or polymer) used together with them. The varying degree of the inclined angle can be generally adjusted by the methods described above.

[0166]

Oriented layers suitable to give a nematic hybrid orientation to a liquid crystalline compound used in the invention include a rubbed oriented layer containing polyimide, a rubbed oriented layer containing polyethersulfone, a rubbed oriented layer containing polyphenylene sulfide, a rubbed oriented layer containing polyethylene terephthalate, a rubbed oriented layer containing polyethylene naphthalate, a rubbed oriented layer containing polyacrylate, and a rubbed oriented layer containing cellulose based plastics.

[0167]

The methods for fixing orientation of the liquid crystalline compounds according used in the invention is described. The liquid crystalline compounds used in the invention is fixed after orientation so as to further stabilize the optical compensation layer of the optical compensation film. It is preferable for the purpose of fixing the orientation that the liquid crystalline compounds

used in the invention have a reactive substituent such as a substituent having an unsaturated bond or a substituent having an active hydrogen at the end of the low molecular weight liquid crystalline molecule for cross-linking between the low molecular weight liquid crystalline compounds or the high molecular weight matrix and the low molecular weight liquid crystalline compound.

[0168]

As the methods for fixing orientation of the liquid crystalline compounds in the invention, all the conventional methods for fixation can be used. Generally, it is preferred that orientation and fixation of the orientation are simultaneously carried out. For example, fixation of the orientation is carried out by forming a liquid crystalline compound layer containing a low molecular weight liquid crystalline compound or a high molecular weight liquid crystalline compound on a support while maintaining at a temperature range (which varies due to kind of liquid crystalline compounds, for example, from room temperature to 100° C) developing its liquid crystal phase, orienting the liquid crystalline compound, and fixing it by cooling to room temperature. The fixation is also carried out by coating a solution, in which a liquid crystalline compound

and another compound are dissolved in a solvent, on an oriented layer, drying the coated layer, heating the dried layer to a temperature developing a nematic phase, fixing the heated layer while maintaining the orientation (nematic phase), and cooling it. The fixation is also carried out by coating a solution, in which a liquid crystalline compound and another compound (for example, a photopolymerizable monomer and a photopolymerization initiator) are dissolved in a solvent, on an oriented layer, drying the coated layer, heating the dried layer to a temperature developing a nematic phase, polymerizing the monomer (for example, by ultraviolet light irradiation).

[0169]

As another method for fixing orientation, there are the following methods: a method of fixing orientation of liquid crystalline compounds wherein a liquid crystalline compound having an unsaturated bond is polymerized optionally in the presence of a photopolymerization initiator or a thermal polymerization initiator by heat or light; a method of fixing orientation of liquid crystalline compounds wherein a mixture of liquid crystalline compounds having in their molecular ends a reactive group such as a substituent having an unsaturated group or a substituent having an active

hydrogen and a polymer matrix is heated, light-irradiated or pH-changed to react; and a method of fixing orientation of liquid crystalline compounds wherein liquid crystalline compounds having a reactive group are cross-linked to another in an individual liquid crystal domain. However, various technique can be applied to the fixation in the invention and is not limited to the above described.

[0170]

The examples of the thermal polymerization initiator include an azo compound, an organic peroxide, an inorganic peroxide, and sulfinic acid. The examples of the photopolymerization initiator include benzophenones, acetophenones, benzoin, and thioxanthenes.

[0171]

The plasticizer, surfactant, or polymerizable monomer as described above may be any, as long as it has compatibility with liquid crystalline compounds used in the invention, changes the inclined angle of liquid crystalline compounds used in the invention, or does not jeopardize orientation. Of these, a polymerizable monomer (for example, a compound having a vinyl group, a vinyloxy group, an acryloyl group or a methacryloyl group) is preferred. The above compounds can be used in an amount of 1 to 50 weight % (preferably 5 to 30



weight %) based on the amount of liquid crystalline compounds used.

[0172]

The polymer as described above may be any, as long as it has compatibility with liquid crystalline compounds used in the invention, or changes the inclined angle of liquid crystalline compounds used in the invention. One example of the polymer is cellulose ester. The preferred examples of the cellulose esters include cellulose acetate, cellulose acetate propionate, hydroxypropyl cellulose and cellulose acetate butyrate. The above polymer can be used in an amount of 0.1 to 10 weight % (preferably 0.1 to 8 weight %, and more preferably 0.1 to 5 weight %) based on the amount of liquid crystalline compounds used, so that it does not jeopardize orientation of the liquid crystalline compounds used. In the cellulose acetate butyrate, the butyrylation degree is 30% or more, and preferably 30 to 80%, and the acetylation degree is 30% or more, and preferably 30 to 80%. The viscosity (according to ASTM D-817-72) of the cellulose acetate butyrate is preferably in the range of from 0.01 to 20 seconds.

[0173]

The layer configuration of the optical compensation film of the present invention will now be described.

The layer configuration of the optical compensation film of the present invention is not particularly limited as long as a layer, comprising uniaxial liquid crystalline compounds, especially positive uniaxial liquid crystalline compounds, is disposed on a biaxial support. In addition to said liquid crystal layer, one or more liquid crystal layers may be disposed. Said liquid crystal layer may be disposed directly on said support. It is possible to commonly provide an orientation layer. Second and following liquid crystal layers may be directly provide on the previously disposed liquid crystal layer (for instance, the first liquid crystal layer). Commonly, it is possible to provide an orientation layer in the same manner as above. It is possible to provide a dissolving-out blocking layer, as described below, between said support and said orientation layer which, is utilized to orient liquid crystals. When a plurality of liquid crystal layers are disposed, it is possible to provide a dissolving-out blocking layer between the first and second liquid crystal layers (when each liquid crystal layer is formed on said orientation layer, between the first liquid crystal layer and the second orientation layer).

[0174]

When these liquid crystal layers are disposed, it is preferable that an antistatic layer be disposed on layer on either side of the support so as to enhance the orientation controlling properties of liquid crystals. Namely, when said optical compensation film is continuously produced in the form of a long optical compensation film, the orientation of liquid crystals is occasionally disturbed due to the static charge formed on the support during the process of contacting conveying rolls or belts and peeling from the same and the like. In order to minimize this drawback, it is very effective to provide said antistatic layer on the support side. An antistatic function may not be disposed to the support side but may be disposed to liquid crystalline compounds thorough addition of materials. In that case, however, it is necessary to choose materials and their concentration so that orientation properties of liquid crystals are not adversely affected.

[0175]

Further, for the purpose of the enhancement of sliding properties, the minimization of blocking, and the like, it is possible to provide a back coat layer on the reverse side of the support, namely on the surface on which no liquid

crystal layer is provide. Further, if desired, it is possible to provide a hard coat layer, a back coat layer, an antistatic layer, an antireflection layer, an antiglare layer, and the like in combination with said back coat layer.

[0176]

The dissolving-out blocking layer according to the present invention will now be described.

In the present invention, liquid crystalline compounds are coated onto a cellulose ester film support according to the present invention. Further, when said orientation layer is disposed between optical compensation layers in which the orientation of said liquid crystalline compounds is fixed, the dissolving-out blocking layer is preferably disposed in order to enhance the adhesion between said cellulose ester film support and said orientation layer.

[0177]

The dissolving-out blocking layer, as described herein, refers to the layer which retards the diffusion of dissolved-out materials from the transparent resinous substrate to the orientation layer or to the optically anisotropic layer comprising liquid crystalline compounds. Said diffusion occurs due to the presence of organic

solvents which are employed to coat the liquid crystalline compounds and to prepare the coating composition of the orientation layer. When said orientation layer as well as said liquid crystalline compound layer is disposed in the form of a thin layer, a method is preferred in which organic solvent solution of these compounds are prepared and then coated. However, transparent resinous substrates such as cellulose ester film supports, and the like, are comprised of resins and often comprised of plasticizers. Organic solvents, which dissolve resins or plasticizers, also dissolve resins in the orientation layer as well as liquid crystalline compounds. As a result, it is readily assumed that during coating, diffusion between layers and contamination between layers occur.

[0178]

During that period, by producing resins which are soluble in solvents which are insoluble or hardly soluble in said organic solvents, it is possible to retard said diffusion between layers as well as said contamination between layers during coating. Further, even though said compounds are soluble in organic solvents which dissolve resins or plasticizers, actinic light hardening resins in the monomer state are applied onto a transparent substrate,

and the resulting coating is subjected to hardening reaction. By so doing, being different from simply coating said layer, it is possible to provide a layer having a dense crosslinked structure. As a result, when resins employed to prepare the orientation layer as well as liquid crystalline compounds are dissolved, it is possible to retard the diffusion and contamination between layers.

[0179]

From the viewpoint of the enhancement of adhesion between the cellulose ester film support and the orientation layer, providing a dissolving-out blocking layer, comprising water-soluble polymers such as, for example, organic acid group containing polymers is effective to enhance production advantages.

[0180]

Listed as organic acid group containing polymers are those having a structure in which the polymer side chain has said organic acid group. However, they are not particularly limited. Listed as organic acid groups is, for example, a -COOH group. Examples of such compounds are not particularly limited. However, listed are, for example, structures represented by General Formulas [1] or [2] described in Japanese Patent Publication Open to Public Inspection No. 7-

333436. The hydrogen atom of a -COOH group may be substituted with ammonia, and alkali metal cations (for example, a sodium cation and a lithium cation). Listed as monomer units, which constitute polymers, having an organic acid group, are acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid and the like. Further, after polymerizing maleic anhydride as the copolymerizable monomer, organic acid groups may be obtained while opening said acid anhydride ring.

[0181]

Listed as one form of said dissolving-out blocking layer in the present invention is the installment of an actinic ray hardening resinous layer. Ultraviolet rays are preferred as said actinic rays due to ease of the procurement of radiation sources as well as related materials.

[0182]

The UV ray hardenable resin includes a UV ray hardenable acrylurethane resin, a UV ray hardenable polyesteracrylate resin, a UV ray hardenable epoxyacrylate resin, a UV ray hardenable polyolacrylate resin and a UV ray hardenable epoxy resin.

[0183]

The UV ray hardenable acrylurethane resin can be obtained by reacting a polyesterpolyol with an isocyanate monomer or its prepolymer and then reacting the resulting product with an acrylate having a hydroxy group such as 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate (hereinafter, the acrylate includes a methacrylate) or 2-hydroxypropylacrylate (Japanese Patent O.P.I. Publication No. 59-151110).

[0184]

The UV ray hardenable polyesteracrylate resin can be obtained by reacting a polyesterpolyol with 2-hydroxyethylacrylate or 2-hydroxypropylacrylate (Japanese Patent O.P.I. Publication No. 59-151112).

[0185]

The example of the UV ray hardenable epoxyacrylate resin includes those obtained by reacting an epoxyacrylate oligomer in the presence of a reactive diluting agent and a photoinitiator (Japanese Patent O.P.I. Publication No. 1-105732). The photoinitiator includes a benzoin derivative, an oxime ketone derivative, a benzophenone derivative or a thioxanthone derivative.

[0186]



The example of the UV ray hardenable polyolacrylate resin includes trimethylolpropane triacrylate, ditrimethylolpropane tetraacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate or alkyl-modified dipentaerythritol pentaerythritol. These resins are usually used with a conventional photoinitiator. The above photoinitiator also works as a photo-sensitizer. The example includes acetophenones, benzophenones, hydroxy benzophenones, Michler's ketone,  $\alpha$ -amylloxime esters, and thioxanthenes or its derivatives. The photo-sensitizers such as n-butylamine, triethylamine and tri-n-butylphosphine can be used in reaction of epoxyacrylates. The content of the photo-initiator or photo-sensitizer used in the ultraviolet ray hardenable resin composition is preferably 0.5 to 5 parts by weight particularly.

[0187]

The coating solution of the ultraviolet ray hardenable resin composition is coated through a gravure coater, a spinner coater, a wire bar coater, a roll coater, a reverse-roll coater, an extrusion coater or an air-doctor coater, and the dry coating thickness is preferably 0.05 to 30  $\mu\text{m}$ , and more preferably 0.1 to 15  $\mu\text{m}$ .

[0188]

Actinic ray hardening resins include those which have at least two polymerizable groups such as a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, an isopropenyl group, an epoxy group, and the like which form a bridge structure or a net structure. Among these active groups, preferred are the acryloyl group, the methacryloyl group or the epoxy group viewed from the aspect of the polymerization rate as well as reactivity, and polyfunctional monomers or oligomers. For example, preferably employed are ultraviolet ray hardening acryl urethane based resins, polyester acrylate based resins, and polyol acrylate based resins.

[0189]

Coating solvents of said dissolving-out blocking layer will now be generally described. In order to achieve the objective of the present invention, it is preferable to choose as coating solvents of said dissolving-out blocking layer solvents which hardly dissolve or do not dissolve resins or plasticizers rather than those which dissolve the same.

[0190]

Said coating solvents are preferably solvent mixtures of at least two organic solvents, which comprise water in an amount of at least 30 percent by weight. Further, the solvent mixture of at least two organic solvents more preferably comprises water in an amount of at least 45 percent by weight. In that case, it is possible to more effectively realize the objective of the present invention. Employed as solvents which are employed together with water, for coating the dissolving-out blocking layer of the present invention, are alcohols, ketones, esters, glycol ethers, and mixtures with other solvents.

[0191]

It is preferable to select organic solvents which are soluble in water. However, a small amount of solvents, which are insoluble in water, may be employed as follows. Said water-insoluble solvent is employed together with at least one of the water-soluble organic solvent and a mixed solvent may be employed which has dissolved at least three components. Herein, alcohols include methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, 2-butanol, tert-butanol, pentanol, 2-methyl-2-butanol, cyclohexanol, and the like. Ketones include acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone, cyclohexanone, and

the like. Esters include methyl formate, ethyl formate, methyl acetate, ethyl acetate, isopropyl acetate, amyl acetate, ethyl lactate, methyl lactate, and the like. Glycol ethers (having from 1 to 4 carbon atoms) include methyl cellosolve, ethyl cellosolve, propylene glycol monomethyl ether (PGME), propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, propylene glycol monoisopropyl ether, propylene glycol monobutyl ether, or propylene glycol monoalkyl (having from 1 to 4 carbon atoms). Alkyl ether esters include propylene glycol monomethyl ether acetate, and propylene glycol monoethyl ether acetate. Solvents other than those include methylene chloride, N-methyl pyrrolidone, and the like. However, said organic solvents are not particularly limited to said compounds.

[0192]

As resins of said dissolving-out blocking layer, nonionic polymers are preferred with respect to the solubility of said solvent mixtures and achieving the objective of the present invention.

[0193]

It is possible to select resins which are soluble in such mixed solvents as the resins of said dissolving-out blocking layer. The structure of resins of said dissolving-

out blocking layer is not particularly limited. For example, it is possible to employ natural polymers as well as semi-synthesized water-soluble polymers.

[0194]

Further, by employing synthesized polymers, it is possible to make them nonionic in terms of the molecular design, being different from natural products. As such compounds, it is possible to employ many types of synthesized polymers such as homopolymers or copolymers of polyvinyl alcohol, partially acetalized polyvinyl alcohol, poly-N-vinylpyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, and the like.

[0195]

Further, as synthesized polymers employed in said dissolving-out blocking layer, monomer units described below may be individually employed or employed in copolymers which are specifically soluble in said solvent mixtures. Specific examples of monomers, forming polymers, include acrylic acid esters, methacrylic acid esters, acrylamides, methacrylamides, crotonic acid esters, vinyl esters, maleic acid esters, fumaric acid esters, itaconic acid esters, olefins, styrens, and the like. Specific examples of these monomers include acrylic acid ester derivatives. Listed as

substituents of these substituted esters are a methyl group, an ethyl group, a n-propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, an amyl group, a hexyl group, a 2-ethylhexyl group, an octyl group, a tert-octyl group, a dodecyl group, a 2-chloroethyl group, a 2-bromoethyl group, a 4-chlorobutyl group, a cyanoethyl group, a 2-acetoxyethyl group, a dimethylaminoethyl group, a benzyl group, a methoxybenzyl group, a 2-chlorocyclohexyl group, a cyclohexyl group, a furfuryl group, a tetrahydrofurfuryl group, a phenyl group, a 5-hydroxypentyl group, a 2,2-dimethyl-3-hydroxypropyl group, a 2-methoxyethyl group, a glycidyl group, an acetoxyethyl group, a 3-methoxybutyl group, a 2-ethoxyethyl group, a 2-iso-propoxy group, a 2-butoxyethyl group, a 2-(2-methoxy)ethyl group, a 2-(2-butoxyethoxy)ethyl group, an  $\omega$ -methoxyoligoxyethylene group (the number of repeated units of oxyethylene:  $n = 7, 9, 11$ , etc.), an  $\omega$ -hydroxyoligoxyethylene group (the number of repeated units of oxyethylene:  $n = 7, 9, 11$ , etc.), a 1-bromo-2-methoxyethyl group, a 1,1-dichloro-ethoxyethyl group, and the like, and acrylic acid esters as well as methacrylic acid esters acrylic acid esters are listed which are constituted, employing these substituents.

[0196]

Further, acrylamide derivatives as well as methacrylamide derivatives include non-substituted acrylamides as well as methacrylamides. Substituents of these substituted amides include a methyl group, an ethyl group, an n-propyl group, an n-butyl group, a tert-butyl group, an n-octyl group, a dodecyl group, a cyclohexyl group, a benzyl group, a hydroxymethyl group, a methoxyethyl group, a dimethylaminopropyl group, a phenyl group, an acetoactoxypropyl group. Listed as N-monosubstituted are a cyanoethyl group and the like. Listed as N,N-disubstituted derivatives are acrylamide derivatives or methacrylamide derivatives having an N,N-diethyl group.

[0197]

Listed as examples of vinyl esters are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl caprate, vinyl chloroacetate, vinyl methoxyacetate, vinyl phenylacetate, vinyl benzoate, vinyl salicylate, and the like.

[0198]

Further, listed as examples of olefins are dichloropentadiene, ethylene, propylene, 1-butene, vinyl

chloride, vinylidene chloride, isoprene, chloroprene, butadiene, 2,3-dimethylbutadiene, and the like.

[0199]

Listed as styrenes are, for example, styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, isopropylstyrene, chloromethylstyrene, methoxystyrene, acetoxystyrene, chlorostyrene, dichlorostyrene, bromostyrene, methyl vinylbenzoate, and the like.

[0200]

Listed as crotonic acid ester are butyl crotonate and hexyl crotonate, and the like.

[0201]

Further, listed as itaconic acid esters are monomethyl itaconate, dimethyl itaconate, monobutyl itaconate, diethyl itaconate, dibutyl itaconate, and the like.

[0202]

Listed as fumaric acid esters are, for example, diethyl fumarate, dimethyl fumarate, dibutyl fumarate, and the like.

[0203]

Listed as example of other monomers are those described below.



Listed as vinyl ketones are, for example, methyl vinyl ketone, phenyl vinyl ketone, methoxyethyl vinyl ketone, and the like.

[0204]

Listed as hetero ring containing vinyl monomers are N-vinylpyridine, 2- and 4-vinylpyridine, vinylimidazole, vinylloxazole, vinyltriazole, N-vinyl-2-pyrrolidone, and the like.

[0205]

Listed unsaturated nitriles are acrylonitrile, methacrylonitrile, and the like.

[0206]

In order to improve adhesion properties, said polymers may comprise in the side chain of said polymers chemically reactive groups such as an unsaturated ethylenic group, an epoxy group, and the like.

[0207]

In the present invention, it is needed that said it is possible to dissolve said polymers in a mixture of at least two organic solvents comprising water in an amount of at least 30 percent by weight, and preferably in an amount of at least 45 percent by weight. As resins of said dissolving-out blocking layer comprised of polymers exhibiting such

dissolving properties, preferred are copolymers containing a ring structure having a hetero atom on the polymer side chain, more preferred are copolymers containing N-vinyl-2-pyrrolidone in an amount of at least 60 percent by weight, and most preferred are homopolymers of N-vinyl-2-pyrrolidone. Further, polyvinyl alcohol is also preferably employed.

[0208]

The higher molecular weight of resins of said dissolving-out blocking layer is preferred due to their minimum diffusion to the orientation layer as well as to the liquid crystal layer. The number average molecular weight is preferably at least 800,000.

[0209]

Further, when said polymers are employed to prepare the dissolving-out blocking layer, the dried layer thickness on a transparent resinous substrate is preferably from 0.1 to 15  $\mu\text{m}$ . When the dried layer thickness is excessively thin, dissolving-out blocking properties are occasionally degraded, while said thickness is excessively thick, the presence of the optical compensation film (also called the optically anisotropic body) on the film occasionally results in curling.

[0210]

Employed as coating methods to apply the organic acid group containing polymer layer, the dissolving-out blocking layer (the layer formed by hardening actinic ray hardening monomers), the orientation layer, and the optically anisotropic layer (the liquid crystal layer) onto the transparent resinous substrate are doctor coating, extrusion coating, slide coating, roll coating, gravure coating, wire bar coating, reverse coating, curtain coating, extrusion coating, or extrusion coating employing a hopper described in U.S. Pat. No. 2,681,294. By employing any of these coating methods, it is possible to carry out coating so as to obtain a dried layer thickness of from 0.1 to 10  $\mu\text{m}$ . It is also possible to adjust said dried layer thickness in accordance with the objective.

[0211]

Said dissolving-out blocking layer is employed for the purpose of minimizing dissolving-out of additives such as plasticizers, UV absorbers, and the like, from the transparent support. In addition to said purpose, said dissolving-out blocking layer is required to exhibit a function of enhancing the adhesion between said support and the optically anisotropic layer or the orientation layer,

and of minimizing peeling. In order to achieve said purposes, the application of a plasma treatment to said transparent resinous substrate is effective. The application of the plasma treatment to said transparent resinous substrate under conveyance makes it possible to carry out a continuous process. Specifically, it is preferable that the film surface undergoes necessary reaction in the presence of reactive gas under an atmospheric pressure without utilizing vacuum.

[0212]

Reactive gases are not particularly limited, and include oxygen, hydrogen, carbon monoxide, carbon dioxide, nitrogen monoxide, nitrogen dioxide, hydrogen peroxide, ozone, and the like. The plasma treatment, as described in the present invention, refers to the utilization of plasma discharge and the generation of a plasma state utilizing discharge. It is preferably carried out by applying voltage to at least two counter electrodes.

[0213]

The treatment system, as described in the present invention, refers to a treatment space in which said plasma discharge is carried out under the presence of said reactive gases, and specifically refers to an treatment room isolated

from the exterior employing partitions such as walls and the like. In the case of a vacuum plasma discharge treatment which is carried out in said treatment room under a pressure of from 0.007 to 27 hPa near true vacuum, it is necessary to regulate the introduction of said reactive gases. In order to increase the rate of treatment, it is necessary to increase the voltage applied to electrodes. However, when the electric field strength excessively increases, a body to be treated may occasionally be damaged. In such a case, caution should be paid.

[0214]

Further, as another embodiment, in the case of an atmospheric pressure plasma treatment, which is carried out under an atmospheric pressure or a near atmospheric pressure, inert gases are preferably introduced to the treatment room together with said active gases so as to generate stable discharge. The atmospheric pressure or the near atmospheric pressure, as described herein, refers to a pressure of from 133 to 1,064 hPa, and preferably from 931 to 1,037 hPa.

[0215]

The inert gases are those which result in no reaction through said plasma discharge, and include argon gas, helium

gas, xenon gas, and krypton gas. Of these, argon gas as well as helium gas is preferred. During the atmospheric pressure plasma treatment, the pressure of introduced inert gases is preferably at least 60 percent, which is more than the ratio of active gases so as to stabilize discharge. When applied voltage is increased, it is possible to increase the rate of treatment. However caution is required so that a body to be treated results in no damage.

[0216]

On the other hand, even in said atmospheric pressure plasma treatment, when plasma is generated utilizing a pulsed electric field, inert gases are not always necessary. Accordingly, it is possible to increase the concentration of reactive gases in said treatment system and to increase the production efficiency.

[0217]

At that time, pulse shapes are not particularly limited and may exhibit pulse shapes shown in Figs. 1(a) through 1(d) of Japanese Patent Publication Open to Public Inspection No. 10-130851.

[0218]

Fig. 1 shows a pulse shape employed in the present invention. The ordinate (V) represents pulse voltage, and

the abscissa ( $t$ ) represents time. Rising time and falling time of said pulse voltage are preferably in the range of from 40 ns to 100  $\mu$ s, respectively. The rising (falling) time, as described herein, refers to time during which, in the pulse shape shown in Fig. 1, voltage starts rising (falling) from the base line and reaches the maximum point (the minimum point). The frequency of pulse electric field is preferably in the range of from 1 to 100 kHz. Time for the application of one pulse electric field is preferably from 1 to 1,000  $\mu$ s. The time for the application of one pulse electric field, as described herein, refers to the time for the application of the pulse having one pulse shape in Fig. 1. The magnitude of voltage, applied to the electrode, results in electric field strength preferably in the range of from 1 to 100 kV/cm. When the applied voltage is high, the rate of treatment increases. However, when the applied voltage is excessively high, a body to be treated results in damage in the same manner as above.

[0219]

Further, in at least two counter electrodes employed in said atmospheric pressure plasma treatment, it is preferable to provide a solid dielectric on the counter side. It is

also preferable to employ sintered ceramics as said dielectric, and the volume resistivity is preferably at least  $10^8 \Omega \cdot \text{cm}$ .

[0220]

The arrangements of the optical compensation film of the present invention will now be detailed with reference to Figs. 2 and 3.

[0221]

It is possible to employ the optical compensation film of the present invention in a TN type TFT liquid crystal apparatus in the various arrangements, as long as it is disposed between the glass of a driving liquid crystal cell or the plastic base material and the polarizing plate. The optical compensation film of the present invention is disposed between the polarizing plate on one surface of said liquid crystal panel and the cell glass or the plastic base material. Further, it is possible to provide said optical compensation film on either the light incident side or the light transmitting side. Though cost increases, said optical compensation film may be disposed on both side.

[0222]

Further, the optical compensation film of the present invention results in difference in a viewing angle



compensation effect, depending on the arrangement direction in the plane, due to the anisotropy in the plane of said optical compensation film. The arrangement method to exhibit said compensation effect is one which realizes the form in which the axis of the maximum refractive index direction of a biaxial support is approximately parallel or approximately orthogonal to the transmission axis of the neighboring polarizing plate. Approximately parallel, as described herein, means that the angle between two of said axes is within  $\pm 10$  degrees, is preferably within  $\pm 3$  degrees, and is still more preferably within  $\pm 1$  degree. Further, approximately orthogonal, as described herein, means that the angle between two of said axes is in the range of from 80 to 100 degrees, is preferably in the range of from 89 to 91 degrees, and is still more preferably in the range of from 89 to 91 degrees. Still further, the approximately parallel arrangement exhibits better compensation effect than the approximately orthogonal arrangement. Figs. 2 and 3 show typical arrangement methods.

[0223]

In Figs. 2 and 3, on liquid cell 6, optical compensation film 3 is placed, and subsequently, polarizing plate 1 is

placed. 7a and 7b are the rubbing axes of a liquid cell, 5 is the rubbing axis of an optical compensation film, 5a and 5b show the rubbing start or end points, 4 shows the maximum refractive index direction of an optically biaxial cellulose ester film support. "2" shows the transmission axis of a polarizing plate.

[0224]

Since the optical compensation film of the present invention comprises a cellulose ester film support forming thereon a liquid crystal layer, there is distinct difference between the two sides, that is the front and the back. Accordingly, when arranged in a liquid cell (or a liquid crystal panel), improvement effects of the viewing angle varies due to the fact that the surface adjacent to the polarizing plate is on the support side or the liquid crystal layer side.

[0225]

Specifically, in terms of said improvement effects, it is more preferable that the side of the optically biaxial cellulose ester film support is arranged on the side of the glass of the liquid cell or plastic base material, namely the side of the liquid crystal layer is arranged on the side adjacent to the polarizing plate. However, in the case of

reversed front and back, the improvement effects are also noted.

[0226]

Further, when the relationship between the average direction of the optical axis of each liquid crystal molecule in a liquid crystal layer and the pre-tilt direction of a liquid cell is expressed utilizing the relationship between the rubbing axis of said liquid crystal cell and said pre-tilt angle, the typical configurations described below are preferably used.

[0227]

First, the following two cases are taken into account and each of them will be described with reference to Figs. 2, 3, 4, and 5: (1) the projection direction in the plane of the optical compensation film in the average direction of the optical direction of each liquid crystal molecule constituting the liquid crystal layer of an optical compensation film is arranged to be approximately parallel to the rubbing direction on the side of a glass or plastic base material adjacent to a liquid crystal cell, and (2) said axes are arranged to be approximately orthogonal to each other.

[0228]

In the case of said (1), when in Fig. 2, the cross-section of said optical compensation film is viewed from the direction of arrow 8, the resultant arrangements are shown as either Fig. 4(a) or Fig. 4(b).

[0229]

In Fig. 4(a), the rubbing direction in optical compensation film 3 in Fig. 2 is shown as the axis directing from 5b to 5a, while in Fig. 4(b), the rubbing direction of the rubbing axis in the optical compensation film in Fig. 2 is shown as the axis directing from 5a to 5b.

[0230]

In this case, the average tilt angle of entire liquid crystal layer 9 of optical compensation film 3 is commonly from 5 to 85 degrees, is preferably from 20 to 70 degrees, and is still more preferably from 30 to 60 degrees. In each of Figs. 4(a) and 4(b), 11 represents orientation configuration. As noted above, said tilt angle may be constant. However, configuration is preferred in which said tilt angle varies continuously or stepwise. Further configuration is acceptable in which said tilt angle increases or decreases toward the air boundary side from the sheet surface side, but the former is preferred.

[0231]

On the other hand, in the case of said (2), when in Fig. 3, the cross-section of the sheet is viewed from the direction of arrow 8, the resultant arrangements are shown as either Fig. 5(a) or Fig. 5(b).

[0232]

In Fig. 5(a), the rubbing direction in optical compensation film 3 in Fig. 3 is shown as the axis directing from 5c to 5d, while in Fig. 5(b), the rubbing direction of the rubbing axis in the optical compensation film in Fig. 3 is shown as the axis directing from 5d to 5c.

[0233]

In this case, the average tilt angle of the entire liquid crystal layer of said optical compensation film 3 is commonly from 5 to 85 degrees, is preferably from 20 to 70 degrees, and is still more preferably from 30 to 60 degrees. In each of Figs. 5(a) and 5(b), 11 represents orientation configuration. As noted above, said tilt angle may be constant. However, configuration is preferred in which said tilt angle varies continuously or stepwise. Further configuration is acceptable in which said tilt angle increases or decreases toward the air boundary side from the sheet surface side, but the former is preferred.

[0234]

Incidentally, the average tilt angle of liquid crystal layer 9 is determined depending on the orientation layer as well as liquid crystal materials, but may be varied utilizing various factors other than these. Specifically, it is possible to readily control the thickness change of the liquid crystal layer. Generally, the tilt angle tends not to be affected by the orientation limiting force of the boundary surface of the orientation layer as well as the air boundary surface. Therefore, for example, when liquid crystal molecules are in the horizontal state in the intermediate region in the thickness direction, said average tilt angle decreases with an increase in the layer thickness. On the other hand, when liquid crystal molecules are in the vertical state in said intermediate region, said tilt angle tends to increase.

[0235]

The liquid crystal display apparatus described will now be described.

Employed as polarizers employed in the polarizing plate of the present invention may be those conventionally known in the art. For example, a film comprised of a hydrophilic polymer such as polyvinyl alcohol, which is treated with dichroic dyes such as iodine and stretched, and a plastic

film such as vinyl chloride, which is subjected to treatment and orientation, are employed. Further, said polarizing plate is constituted in such a manner that the compensation film of the present invention is laminated onto at least one side of the polarizer. When laminated onto only one side, it may be possible to use either the cellulose ester film support according to the present invention, having no coated liquid crystal layer on the other side, other transparent supports, or TAC (triacetate) film.

[0236]

The polarizing plate, obtained as above, is disposed on either one side or on both sides of the liquid crystal cell. When disposed on one side, it is possible to obtain the liquid crystal display apparatus of the present invention by adhering the optical compensation film of the present invention to the place which is nearer the liquid crystal cell with respect to the polarizer.

[0237]

#### [EXAMPLES]

The present invention will now be detailed with reference to examples. However, the present invention is not to be construed as being limited to these examples.

[0238]

## Example 1

## «Preparation of Optical Compensation Films 1A and 1B»

Each of Optical Compensation Films 1A and 1B was prepared as described hereunder.

[0239]

## «Preparation of Cellulose Ester Film Support 1»

Charged into a tight-sealed vessel were 100 weight parts of cellulose acetate propionate having a degree of acetyl group substitution of 2.00, a degree of propionyl substitution of 0.80, and a viscosity average degree of polymerization of 350, 5 weight parts of ethylphthalyl ethyl glycolate, 3 weight parts of triphenyl phosphate, 290 weight parts of methylene chloride, and 60 weight parts of ethanol, and the resultant mixture was heated while slowly stirred. Then, dissolution was carried out while being heated to 45 °C over 60 minutes. Interior pressure of said vessel became 1.2 atmospheric pressures. The resultant dope was filtered employing Azumi Filter Paper No. 244, manufactured by Azumi Filter Paper Co., Ltd. . Afterward, the filtered dope was kept at a still state for 24 hours to allow bubbles to dissipate. Further, separately, 5 weight parts of said cellulose acetate propionate, 6 weight parts of Tinuvin 326 (manufactured by Ciba Specialty Chemicals Co., Ltd.), 4



weight parts of Tinuvin 109 (also manufactured by Ciba Specialty Chemicals Co., Ltd.), 5 weight parts of Tinuvin 171 (again manufactured by Ciba Specialty Chemicals Co., Ltd.) were mixed with 94 weight parts of methylene chloride, and 8 weight parts of ethanol were mixed and dissolved while stirring, whereby a UV absorber solution was prepared. Then, blending was carried out at a ratio of 100 weight parts of said dope to 2 weight parts of said UV absorber solution. After sufficiently mixing the resultant blend employing a static mixer, the resultant dope maintained at 30 °C was cast onto a stainless steel belt from a die. Subsequently, drying was carried out for one minute on said belt of which back surface was subjected to temperature regulation through contact of 25 °C heated water. Thereafter, chilling was carried out for 15 seconds on said belt of which back surface came into contact with 15 °C chilled, and peeling from said belt was then carried out. The residual solvent in the web during peeling was 100 percent by weight. Subsequently, both edges of the peeled web were clipped employing a simultaneous biaxially stretching tenter, and by simultaneously varying the distance between the clips in the width direction as well as in the casting direction (in the

length direction), stretching was carried out at 120 °C by a factor of 1.65 in the width direction and by a factor of 1.1 in the casting direction (in the length direction). After stretching, the resultant film was temporarily cooled to 80 °C. Afterward, said film was stretched at 130 °C by a factor of 1.1 in the length direction, employing rollers rotated at different circumferential speeds. The resultant film was dried at 130 °C for 10 minutes while being roller-conveyed, whereby a 100  $\mu\text{m}$  thick cellulose ester film (Cellulose Ester Film Support 1) was obtained.

[0240]

Said Cellulose Ester Film Support 1 was wound onto a 200 mm diameter and 1 m wide glass fiber reinforced resin core, to form a 1,000 m long film roll, utilizing a taper tensioning method. During said winding, knurling treatment was carried out by forcedly contacting the film edge with an embossing ring kept at 250 °C, whereby close contact of said film is minimized.

[0241]

Samples were obtained from the central area in the film width direction of the obtained roll film. Refractive index  $N_x$  in the lagging phase axis direction, refractive index  $N_y$

in the leading phase axis direction, and refractive index  $N_z$  in the thickness direction were determined as described below, and  $R_o$  and  $R_t$  were calculated employing formulas also described below, whereby at said central area, values of 84.0 nm and 175 nm were obtained, respectively.

[0242]

$$R_o = (N_x - N_y) \times d$$

$$R_t = [(N_x + N_y)/2 - N_z] \times d$$

Here "d" represents the thickness (in nm) of the film.

Further, it was found that the delayed phase axis direction of each sample was within the range of 1.6 degrees with respect to the film width direction.

[0243]

Three-dimensional refractive indices were obtained at 25 °C and 55 percent relative humidity, employing an automatic birefringence meter KOBRA-21ADH (manufactured by Oji Keisokukiki Co., Ltd.), and values for refractive indices  $N_x$ ,  $N_y$ , and  $N_z$  were obtained. Further, the moisture content was determined employing the method described below, resulting in 1.8 percent.

[0244]

«Method for Measuring Moisture Content»

Said cellulose ester film sample was cut into 10 cm<sup>2</sup> pieces, and was set aside under 23 °C and 80 percent relative humidity for 48 hours. Thereafter, the weight was measured and was termed "W1". Subsequently, after said film sample was subjected to heating and drying treatment at 120 °C for 45 minutes, the weight was again measured and was termed "W2". The moisture content at 23 °C and 80 percent relative humidity was determined by the calculation formula below, employing each of the two measurement values.

[0245]

$$\text{Moisture content (in percent)} = [(W1 - W2)/W2] \times 100$$

«Preparation of Orientation Layer A»

Subsequently, an orientation layer was applied onto Cellulose Ester Film Support 1 employing the method described below and said orientation layer was prepared as described below.

[0246]

(Preparation of Orientation Layer "A")

A thin gelatin layer (at a thickness of 0.1 μm) was applied onto said Cellulose Ester Film Support 1, and onto the resulting gelatin layer applied was a methanol/water = 1 : 4 solution of straight chain alkyl modified polyvinyl

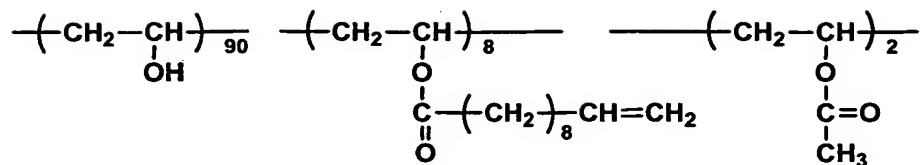
alcohol (MP203, manufactured by Kuraray Co., Ltd.), employing a #3 wire bar. After drying the coating, employing heated air at 80 °C, a rubbing treatment was carried out in the direction which is orthogonal to the direction of the maximum refractive index of Cellulose Ester Film Support 1, whereby an orientation layer was formed. The resultant layer was designated as Orientation Layer "A".

[0247]

(Preparation of Orientation Layer "B")

A thin gelatin layer (at a thickness of 0.1  $\mu\text{m}$ ) was applied onto said Cellulose Ester Film Support 1, and onto the resulting gelatin layer, applied was an alkyl modified polyvinyl alcohol having the structure shown below:  
methanol/water = 1 : 4 solution, employing a #3 wire bar. After drying the coating, employing heated air at 65 °C, a rubbing treatment was carried out in the direction which is orthogonal to the direction of the maximum refractive index of Cellulose Ester Film Support 1, whereby an orientation layer was formed. The resultant layer was designated as Orientation Layer "B".

[0248]



[0249]

Regarding the direction of the optical compensation film which has been subjected to a rubbing treatment, when an orientation layer applied support is viewed from the surface of the orientation layer, the linear rubbing direction is regarded as the + direction of the Y axis, and the X axis, which is orthogonal to said Y axis, is arranged within the support surface, and the resultant arrangement is determined as the standard one. Thereafter, when the plane direction of the surface of said optical compensation film is specified, the rubbing direction is determined as the standard, unless otherwise specified.

[0250]

Characteristics of Orientation Films "A" and "B", as well as orientation characteristics of liquid crystalline compounds obtained by the combination of liquid crystalline compounds were determined employing the steps described below.

Each orientation layer (each type of A and B) and each of Solutions LC-1 and LC-2 described below were combined,

and characteristics of each orientation layer were examined. It was found that regarding liquid crystalline properties of liquid crystalline compound solutions LC-1 and LC-2, each formed an enantiotropic nematic layer.

[0251]

Orientation characteristics were examined employing the methods described below. Each orientation treatment was applied to an orientation layer-coated slide glass. After applying solutions LC-1 and LC-2 onto said orientation layer, solvents were removed by drying, whereby said orientation layer was adjusted to be anti-parallel. Further, employing a hot stage, an orthoscope image and a conoscope image were observed in the liquid crystal temperature range. Further, the average tilt angle when an anti-parallel treatment was carried out, was determined employing an automatic birefringence meter.

[0252]

Further, samples were prepared in which the orientation layer comprised of liquid crystalline compounds was formed on only one surface by applying Solutions LC-1 and LC-2 onto each orientation layer, and subsequently, drying and thermally treating the resulting coating, and the other surface became an air boundary. Obtained samples were

observed and measured in the same manner as described above, and an average tilt angle, which was obtained by the combination of liquid crystalline compounds and the orientation layer, was determined.

[0253]

All hardened layers comprising each liquid crystalline compound were an 0.9  $\mu\text{m}$  thick optically anisotropic layer. The average tilt angle of these films was determined employing KOBRA, manufactured by Oji Keisoku.

[0254]

(Composition of LC-1)

MEK	89.5 parts
Compound 1	2 parts
Compound 2	4 parts
Compound 3	3 parts
Irugacure 369 (manufactured by Ciba	
Specialty Chemicals)	1.5 parts

(Composition of LC-2)

MEK	89.5 parts
Compound 1	3 parts
Compound 2	3 parts
Compound 3	5 parts
Irugacure 369 (manufactured by Ciba	

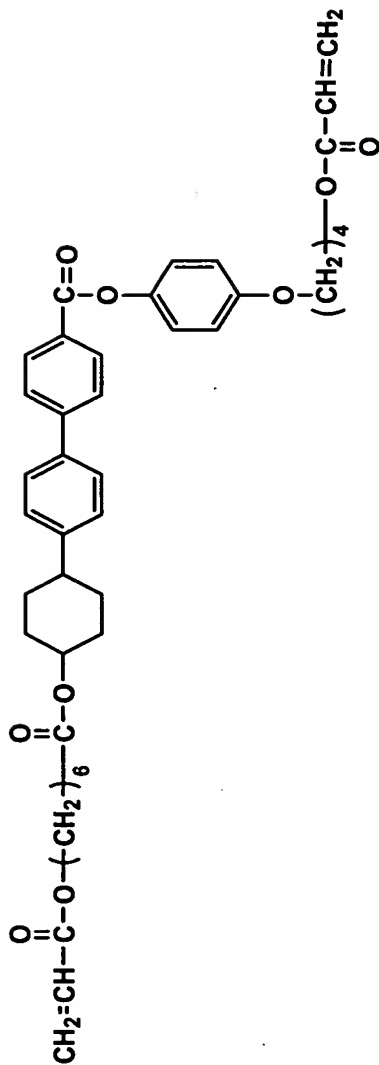


Specialty Chemicals)

1.5 parts

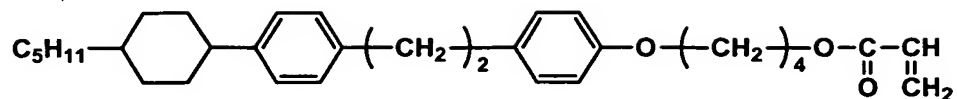
[0255]

Compound 1



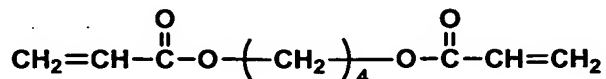
[0256]

Compound 2



[0257]

Compound 3



[0258]

Orientation Layer	Liquid Crystal Solution	Anti-parallel Treatment	Average Tilt Angle
A	LC-1	4°	36°
A	LC-2	4°	7°
B	LC-1	homeotropic	83°
B	LC-2	homeotropic	47°

These results showed that each of the pre-tilt angles of Orientating Layers "A" and "B" was no more than about 5 degrees and at least 80 degrees, respectively, and Solution LC-1 resulted in a high tilt angle at the air boundary surface, while LC-2 resulted in a low tilt angle at the air boundary surface.

[0259]

«Preparation of an Optical Compensation Film»

Subsequently, an optical compensation film was prepared as described hereunder.

[0260]

(Preparation of Optical Compensation Film "1A")

Applied onto Orientation Layer "A", prepared as above, was said Solution LC-1 employing a #5 wire bar. Further, the resultant coating was dried in still air at 55 °C for 30 seconds, and thermally treated at 75 °C for 30 seconds. After carrying out a nitrogen purge at 98 kPa for 60 seconds, a layer was prepared which was hardened employing ultraviolet rays of 450 mJ/cm<sup>2</sup>, under an oxygen concentration of 0.1 percent. Optical Compensation Film "1B" was obtained, comprised of one liquid crystal orientation layer obtained as above.

[0261]

(Preparation of Optical Compensation Film "1B")

Applied onto Orientation Layer "B" prepared as above was said Solution LC-2 employing a #5 wire bar. Further, the resultant coating was dried in still air at 55 °C for 30 seconds, and thermally treated at 75 °C for 30 seconds. After carrying out a nitrogen purge at 98 kPa for 60 seconds, a layer was prepared which was hardened employing

ultraviolet rays of  $450 \text{ mJ/cm}^2$ , under an oxygen concentration of 0.1 percent. Optical Compensation Film "1B" was obtained, comprised of one liquid crystal orientation layer obtained as above.

[0262]

The viewing angle of Optical Compensation Films "1A" and "1B" was determined employing the method described below.

[0263]

Each of Optical Compensation Films "1A" and "1B" was arranged between a glass substrate, on the observer's side, and a polarizing plate, and was adhered, as described below. Evaluation was carried out employing a panel. Said optical compensation film was arranged so that the liquid crystal side came into contact with a support, and the rubbing direction on the substrate surface near said liquid cell was equal to the rubbing axis-Y direction of Optical Compensation Films "1A" and "1B" of the present invention, and adhesion was carried out so that said rubbing axis was orthogonal to the transmission axis of the polarizing plate. Employed as the liquid cell were those which were obtained by peeling the optical compensation film and the polarizing plate which had been adhered to a 15-inch Display Multi-Sync LCD 1525J, manufactured by NEC. The viewing angle of said

liquid crystal panel pasted to the optical compensation film, prepared as above, was determined employing EZ-contrast manufactured by Eldim Co. Said viewing angle was expressed employing a range of inclination angle from the normal line direction against the panel surface which exhibited a contrast ratio of at least 10 of the white display to the black display of the liquid crystal panel. Table 1 shows the values of viewing angles obtained in the optical compensation film of the present invention.

[0264]

«Preparation of Optical Compensation Films "2A" and "2B"»

Charged into a tightly sealed vessel were 100 weight parts of cellulose acetate propionate having a degree of acetyl group substitution of 1.60, a degree of propionyl substitution of 1.20, and a viscosity average degree of polymerization of 400, 5 weight parts of ethylphthalyl ethyl glycolate, 3 weight parts of triphenyl phosphate, 290 weight parts of methylene chloride, and 60 weight parts of ethanol, and the resultant mixture was heated while slowly stirred. Then, dissolution was carried out while being heated to 45 °C over 60 minutes. Interior pressure of said vessel became 1.2 atmospheric pressures. The resultant dope was filtered employing Azumi Filter Paper No. 244, manufactured by Azumi

Filter Paper Co., Ltd. . Afterward, the filtered dope was set aside for 24 hours to allow bubbles to dissipate. Further, separately, 5 weight parts of said cellulose acetate propionate, 6 weight parts of Tinuvin 326 (manufactured by Ciba Specialty Chemicals Co., Ltd.), 4 weight parts of Tinuvin 109 (also manufactured by Ciba Specialty Chemicals Co., Ltd.), 1 weight part of Tinuvin 171 (again manufactured by Ciba Specialty Chemicals Co., Ltd.), and 1 weight part of Aerosil R972V (manufactured by Nippon Aerosil Co., Ltd.) were mixed with 94 weight parts of methylene chloride, and 8 weight parts of ethanol and dissolved while stirred, whereby a UV absorber solution was prepared. Then, blending was carried out at a ratio of 100 weight parts of said dope to 2 weight parts of said UV absorber solution. After sufficiently mixing the resultant blend, employing a static mixer, the resultant dope, at 30 °C, was cast onto a stainless steel belt from a die. Subsequently, drying was carried out for one minute on said belt of which opposite surface was subjected to temperature regulation through the contact of 25 °C heated water. Thereafter, chilling was carried out for 15 seconds on said belt of which back surface came into contact with 15 °C

chilled water, and peeling from said stainless steel belt was then carried out. The residual solvent in the web during separation was 100 percent by weight. Subsequently, both edges of the peeled web were clipped employing a simultaneous biaxially stretching tenter, and by simultaneously varying the distance between said clips in the width direction, as well as in the casting direction (in the length direction), stretching was carried out at 120 °C by a factor of 1.2 in the width direction and by a factor of 1.05 in the casting direction (in the length direction). After stretching, the resultant film was temporarily cooled to 80 °C. Afterward, said film was stretched at 130 °C by a factor of 1.1 in the length direction, employing rollers rotated at different circumferential speeds. The resultant film was dried at 130 °C for 10 minutes while being roller-conveyed, whereby a 100 µm thick cellulose ester film (Cellulose Ester Film Support "a2") was obtained.

[0265]

Said Cellulose Ester Film Support "a2" was wound onto a 200 mm diameter and 1 m wide glass fiber reinforced resin core in the form of a 1,000 m long film roll, utilizing a taper tensioning method. During said winding, knurling

treatment was carried out by forcedly contacting the film edge with an embossing ring kept at 250 °C, whereby close contact of said film was minimized.

[0266]

Samples were obtained from the central area in the film width direction of the obtained film roll. Refractive index  $N_x$  in the lagging phase axis direction, refractive index  $N_y$  in the leading phase axis direction, and refractive index  $N_z$  in the thickness direction, were determined in the same manner as the case in which Optical Compensation Films "1A" and 1B, was prepared and evaluated, and  $R_o$  and  $R_t$  were calculated, whereby 34.0 nm and 175 nm, at the central area, were obtained, respectively.

[0267]

Further, it was found that the direction of the lagging phase axis was within the range of  $\pm 1.3$  degrees. The resulting moisture content, which was determined according to said method, was 2.1 percent.

[0268]

By employing said support, an orientation layer was prepared on said support in the same manner as in the preparation of Optical Compensation Films "1A" and "1B", and



subsequently, crystalline compounds were applied onto the resultant orientation layer, whereby Optical Compensation Films "2A" and "2B" were obtained. Incidentally, the direction of a rubbing treatment, which was applied to said optical compensation film, was determined in the same manner.

[0269]

Subsequently, the viewing angle of prepared Optical Compensation Films 2A and 2B was determined. Table 1 shows the obtained viewing angles.

[0270]

«Preparation and Evaluation of Optical Compensation Films "3A" and "3B"»

Charged into a tightly sealed vessel were 100 weight parts of cellulose acetate propionate having a degree of acetyl group substitution of 2.30, a degree of propionyl substitution of 0.5, and a viscosity average degree of polymerization of 300, 5 weight parts of ethylphthalyl ethyl glycolate, 3 weight parts of triphenyl phosphate, 290 weight parts of methylene chloride, and 60 weight parts of ethanol, and the resultant mixture was heated while slowly stirred. Then, dissolution was carried out while being heated to 45 °C

over 60 minutes. Interior pressure of said vessel became 1.2 atmospheric pressures.

[0271]

The resultant dope was filtered employing Azumi Filter Paper No. 244, manufactured by Azumi Filter Paper Co., Ltd. . Afterward, the filtered dope was set aside for 24 hours to allow to dissipate bubbles. Further, mixed separately were 5 weight parts of said cellulose acetate propionate, 3 weight parts of Tinuvin 326 (manufactured by Ciba Specialty Chemicals Co., Ltd.), 4 weight parts of Tinuvin 109 (also manufactured by Ciba Specialty Chemicals Co., Ltd.), and 5 weight parts of Tinuvin 171 (again manufactured by Ciba Specialty Chemicals Co., Ltd.) added to 90 weight parts of methylene chloride and 10 weight parts of ethanol, and dissolved while stirring, whereby a UV absorber solution was prepared.

[0272]

Blending was then carried out at a ratio of 100 weight parts of said dope to 2 weight parts of said UV absorber solution. After sufficiently mixing the resultant blend employing a static mixer, the resultant dope maintained at 35 °C was cast onto a stainless steel belt from a die. Subsequently, drying was carried out for one minute on said

belt of which opposite surface was subjected to temperature regulation through the contact of 35 °C heated water.

Thereafter, chilling was carried out for 15 seconds on said belt of which back surface came into contact with 15 °C chilled water, and peeling from said stainless steel belt was carried out. The residual solvent in the web during peeling was 70 percent by weight.

[0273]

Subsequently, while conveying said web through a 120 °C oven employing rolls, stretching by a factor of 2.7 in the casting direction (the film length direction) was carried out by setting the circumferential speed of the rolls at the end of said oven to be 2.7 times higher than that of the roll at the beginning of said oven. After stretching, said web was immediately cooled to 60 °C. Further, both edges of said web were clipped employing a tenter, and while maintaining the distance between clips, said web was dried at 140 °C for 5 minutes, whereby a 165 µm thick cellulose ester film (Cellulose Ester Film support 3) was obtained.

[0274]

Said Cellulose Ester Film Support 3 was wound on a 200 mm diameter and 1 m wide glass fiber reinforced resin core

into the form of 1,000 m long film roll, utilizing a taper tensioning method. During said winding, a knurling treatment was carried out by forcedly contacting the film edges with a 270 °C embossing ring, whereby close contact of said film was minimized.

[0275]

Samples were obtained from the central area in the film width direction of the obtained roll film. Refractive index  $N_x$  in the lagging phase axis direction, refractive index  $N_y$  in the leading phase axis direction, and refractive index  $N_z$  in the thickness direction were determined in the same manner as above, and  $R_o$  and  $R_t$  were calculated, whereby, at the central area, 197 nm and 155 nm were obtained, respectively.

[0276]

Further, it was found that the lagging phase axis direction with respect to the length direction (the casting direction) was 0 degree at the center in the film width direction, and from 0.9 to -0.9 degree at the edges. The moisture content, which was measured according to said method, resulted in 2.0 percent.

[0277]

By employing the resultant support, an orientation layer was applied onto said support in the same manner as in the preparation of Optical Compensation Films "1A" and "1B", and subsequently, crystalline compounds were applied onto the resultant orientation layer, whereby Optical Compensation Films "3A" and "3B" were obtained.

[0278]

Incidentally, the direction of a rubbing treatment, which was applied to said optical compensation film, was determined in the same manner.

The viewing angle of prepared Optical Compensation Films "3A" and "3B" was determined employing the same method as previously described. Table 1 shows the obtained viewing angles.

[0279]

«Preparation of Optical Compensation Films "4A" and "4B"»

Cellulose Ester Film Support 4, at a thickness of 100  $\mu\text{m}$ , as well as its film roll was prepared in the same manner as Optical Compensation Films "1A" and "1B", except that cellulose ester employed to prepare said cellulose ester film support was replaced with one having a degree of acetyl group substitution of 1.90, a degree of butyryl substitution

of 0.75, and a viscosity average degree of polymerization of 300.

[0280]

Samples were obtained from the central area in the film width direction of the obtained roll film. Refractive index  $N_x$  in the lagging phase axis direction, refractive index  $N_y$  in the leading phase axis direction, and refractive index  $N_z$  in the thickness direction were determined in the same manner, and  $R_o$  and  $R_t$  were calculated, whereby at the central area, 150 nm and 135 nm were obtained, respectively.

[0281]

Further, it was found that the lagging phase axis direction with respect to the width direction was 0 degree at the center in the film width direction, and from 5 to -5 degrees at the edges. The moisture content, which was measured according to said method, resulted in being 1.3 percent.

[0282]

By employing the resultant support, an orientation layer was applied onto said support in the same manner, and subsequently, crystalline compounds were applied onto the resultant orientation layer, whereby Optical Compensation Films "4A" and "4B" were obtained.

[0283]

Incidentally, the direction of a rubbing treatment, which was applied to said optical compensation film, was determined in the same manner. The viewing angle of prepared Optical Compensation Films "4A" and "4B" was determined.

[0284]

Table 1 shows the obtained viewing angles.

«Preparation of Optical Compensation Films "5A" and "5B"»

Charged into a tightly sealed vessel were 100 weight parts of cellulose acetate propionate having a degree of acetyl group substitution of 2.00, a degree of propionyl substitution of 0.80, and a viscosity average degree of polymerization of 350, 5 weight parts of ethylphthalyl ethyl glycolate, 3 weight parts of triphenyl phosphate, 175 weight parts of methyl acetate, and 75 weight parts of ethanol, and the resultant mixture was heated while slowly stirred. Then, dissolution was carried out while being heated to 65 °C over 60 minutes. Interior pressure of said vessel became 1.2 atmospheric pressures. The resultant dope was filtered employing Azumi Filter Paper No. 244, manufactured by Azumi Filter Paper Co., Ltd. . Afterward, the filtered dope was set side for 24 hours to allow bubbles to dissipate. Further, separately, 5 weight parts of said cellulose

acetate propionate, 6 weight parts of Tinuvin 326 (manufactured by Ciba Specialty Chemicals Co., Ltd.), 4 weight parts of Tinuvin 109 (also manufactured by Ciba Specialty Chemicals Co., Ltd.), 5 weight parts of Tinuvin 171 (again manufactured by Ciba Specialty Chemicals Co., Ltd.), were mixed with 94 weight parts of methyl acetate and 8 weight parts of ethanol, and dissolved while stirring, whereby a UV absorber solution was prepared. Then, blending was carried out at a ratio of 100 weight parts of said dope to 2 weight parts of said UV absorber solution. After sufficiently mixing the resultant blend, employing a static mixer, the resultant dope was cast at 50 °C onto a stainless steel belt from a die. Subsequently, drying was carried out for one minute on said belt of which back surface was subjected to temperature regulation through the contact 55 °C heated water. Thereafter, chilling was carried out for 15 seconds on said belt of which back surface came into contact with 15 °C chilled water, and peeling from said belt was then carried out. The residual solvent in the web during peeling was 70 percent by weight. Subsequently, both edges of the peeled web were clipped employing a simultaneous biaxially stretching tenter, and by simultaneously varying the



distance between clips in the width direction as well as in the casting direction (in the length direction), stretching was carried out at 190 °C by a factor of 1.9 in the width direction and by a factor of 1.05 in the casting direction (in the length direction). After stretching, the resultant film was temporarily cooled to 80 °C. Afterward, said film was stretched at 130 °C by a factor of 1.05 in the length direction, employing rollers rotated at different circumferential speeds. Further, the resultant film was dried at 130 °C for 10 minutes while being conveyed employing rollers, whereby a 120  $\mu$ m thick cellulose ester film (Cellulose Ester Film Support 5) was obtained.

[0285]

Said Cellulose Ester Film Support 5 was wound onto a 200 mm diameter and 1 m wide glass fiber reinforced resin core in the form of 1,000 m long film roll, utilizing a taper tensioning method. During said winding, a knurling treatment was carried out by forcedly contacting the film edges with a 250 °C embossing ring, whereby close contact of said film was minimized.

[0286]

Samples were obtained from the central area in the film width direction of the obtained roll film. Refractive index  $N_x$  in the lagging phase axis direction, refractive index  $N_y$  in the leading phase axis direction, and refractive index  $N_z$  in the thickness direction were determined in the same manner as above, and  $R_o$  and  $R_t$  were calculated, whereby 165.0 nm and 185 nm were obtained, respectively.

[0287]

Further, it was found that the direction of the lagging phase axis of each sample was within the range of  $\pm 1$  degree. The moisture content, which was determined according to said method, resulted in being 1.6 percent.

[0288]

By employing the resultant support, an orientation layer was prepared on said support in the same manner, and subsequently, crystalline compounds were applied onto the resultant orientation layer, whereby Optical Compensation Films "5A" and "5B" were obtained.

[0289]

Incidentally, the direction of a rubbing treatment which was applied to said optical compensation film was determined in the same manner. Subsequently, the viewing

angle of prepared Optical Compensation Films "5A" and "5B" was determined.

[0290]

Table 1 shows the obtained viewing angle values.

Further, as a comparative example, the previously adhered optical compensation film, in a 15-inch display Multi Sync LCD1525J manufactured by NEC, was peeled off and the cellulose ester film (being Protective Film 1 which exhibited no optical biaxial properties) described in Example 2 was alternatively adhered. The viewing angle of said comparative example was measured in the same manner as said Optical Compensation Films "1A" and "1B".

[0291]

(Table 1)

Optical Compensation Film Sample No.	Viewing Angle Left	Viewing Angle Right	Viewing Angle Upper	Viewing Angle Lower	Remarks
1A	60°	60°	45°	30°	Present Invention
1B	60°	60°	40°	30°	Present Invention
2A	60°	60°	40°	30°	Present Invention
2B	60°	60°	40°	30°	Present Invention
3A	65°	65°	45°	30°	Present Invention
3B	60°	60°	45°	30°	Present Invention
4A	65°	65°	40°	35°	Present Invention
4B	60°	60°	45°	30°	Present Invention
5A	65°	65°	45°	35°	Present Invention
5B	60°	60°	40°	30°	Present Invention
Protective Film 1	35°	35°	25°	20°	Comparative Example

[0292]

As can be clearly seen from Table 1, the optical compensation films of the present invention result in markedly pronounced improvement of the viewing angle compared to the Comparative Example.

[0293]

## Example 2

## «Preparation of Polarizing Plate»

## (Preparation of Protective Film 1)

Charged into a tightly sealed vessel were 100 weight parts of cellulose triacetate having a degree of acetyl group substitution of 2.92 and a viscosity average degree of polymerization of 300, 2 weight parts of ethylphthalyl ethyl glycolate, 10 weight parts of triphenyl phosphate, 350 weight parts of methylene chloride, and 50 weight parts of ethanol, and the resultant mixture was heated while slowly stirred. Then, dissolution was carried out while being heated to 45 °C over 60 minutes. Interior pressure of said vessel became 1.2 atmospheric pressures.

[0294]

The resultant dope was filtered employing Azumi Filter Paper No. 244, manufactured by Azumi Filter Paper Co., Ltd. . Afterward, the filtered dope was set aside for 24 hours to allow bubbles to dissipate.

[0295]

Further, separately, 5 weight parts of said cellulose triacetate, 3 weight parts of Tinuvin 326 (manufactured by Ciba Specialty Chemicals Co., Ltd.), 7 weight parts of Tinuvin 109 (manufactured by Ciba Specialty Chemicals Co.,

Ltd.), 5 weight parts of Tinuvin 171 (manufactured by Ciba Specialty Chemicals Co., Ltd.), and 1 weight part of Aerosil 200V (manufactured by Nippon Aerosil Co., Ltd.) were mixed with 90 weight parts of methylene chloride and 10 weight parts of ethanol, and dissolved while stirring, whereby a UV absorber solution was prepared. Then, blending was carried out at a ratio of 100 weight parts of said dope to 2 weight parts of said UV absorber solution. After sufficiently mixing the resultant blend employing a static mixer, the resultant dope was cast at 35 °C onto a stainless steel belt from the die. Subsequently, drying was carried out for one minute on said belt of which back surface was subjected to temperature regulation through the contact of 35 °C heated water. Thereafter, chilling was carried out for 15 seconds on said belt of which back surface came into contact with 15 °C chilled water, and peeling from said belt was then carried out.

[0296]

The residual solvent in the web during peeling was 70 percent by weight. Subsequently, both edges of the peeled web were fixed and drying was carried out at 120 °C for 10

minutes, whereby an 80  $\mu\text{m}$  thick cellulose ester film (Protective Film 1) was obtained.

[0297]

Each of Optical Compensation Films "5A" and "5B" obtained in Example 1 was immersed in a 2 mol/liter sodium hydroxide solution at 60 °C for 2 minutes, washed with water for 2 minutes, and subsequently dried at 100 °C for 10 minutes, whereby an alkali saponified cellulose ester film was obtained.

[0298]

Further, a 120  $\mu\text{m}$  thick polyvinyl alcohol film was immersed in 100 weight parts of an aqueous solution containing 1 weight part of iodine and 4 weight parts of boric acid, and was stretched by a factor of 4 at 50 °C, whereby a polarizing layer (Polarizer 1) was prepared.

[0299]

Each of polarizing plates (Polarizing Plates "A" and "B") was prepared in such a manner that one surface of said Polarizer 1 was adhered to the surface of the support of each of Optical Compensation Films "5A" and "5B", of which one surface had been alkali-saponified in the same manner as said back surface of Protective Film 1, employing as the

adhesive a 5 percent aqueous solution of completely saponified type polyvinyl alcohol. Adhesion was carried out in such a manner that the angle between the polarizing axis of said polarizer and the width direction of said cellulose ester film support was adjusted so that the absorption axis of said polarizing axis was parallel to the rubbing axis of said optical compensation film.

[0300]

The polarizing plate prepared as above was arranged and adhered onto the substrate surface on the side of the operator who observed the liquid cell so that the rubbing direction on the said substrate surface was the same as the +Y direction of Optical Compensation Films "5A" and "5B". Further, a polarizing plate, which was prepared employing only Protective Film 1 on the back surface of said liquid cell, was arranged to be parallel to the rubbing axis near the transmission axis.

[0301]

Further, the direction of the rubbing treated optical compensation film was determined according to Example 1.

[0302]

The viewing angle of the liquid crystal panel, adhered to prepared Polarizing Plates "A" and "B", was determined



employing the method of Example 1. The table below shows obtained viewing angles of the polarizing plates of the present invention.

[0303]

	Viewing Angle			
	Left	Right	Upper	Lower
Liquid Crystal Panel (employing Polarizing Plate "A")	60°	60°	40°	30°
Liquid Crystal Panel (employing Polarizing Plate "B")	60°	60°	40°	30°
Comparative (employing Protective Film 1)	35°	35°	25°	20°

As can be clearly seen from the above table, the polarizing plates of the present invention resulted in markedly pronounced improved effects of the viewing angle compared to Comparative Liquid Crystal Panel which is comprised of the protective film described in Example 1.

[0304]

#### [EFFECTS OF THE INVENTION]

According to the present invention, it is possible to provide an optical compensation film which readily improves viewing angle properties of TN type LCD such as TN-TFT, and the like, that is, image area contrast, coloring, and reversal phenomena of light-and-shadow, which are obliquely viewed, and further, to provide a polarized plate and a

liquid crystal display apparatus with marked improvement of the viewing angle under a simplified constitution, while employing said optical compensation film.

[BRIEF DESCRIPTION OF THE DRAWINGS]

Fig. 1 shows a pulse shape of voltage applied to an electrode which can be applied to an atmospheric pressure plasma discharge treatment in the present invention.

Fig. 2 shows one example of an arrangement form in which the optical compensation film of the present invention is employed.

Fig. 3 shows one example of an arrangement form in which the optical compensation film of the present invention is employed.

Figs. 4(a) and 4(b) are cross-sectional views of the optical compensation film installed in a liquid crystal panel.

Figs. 5(a) and 4(b) are cross-sectional views of the optical compensation film installed in a liquid crystal panel.

[DESCRIPTION OF NUMERALS AND SYMBOL]

1 polarizing plate

2 transmission axis of polarizing plate

3 optical compensation film

4 direction of maximum refractive index of cellulose ester  
film support

5 rubbing axis of optical compensation film

6 liquid cell

[ NAME OF THE DOCUMENT ] Drawings



FIG. 1

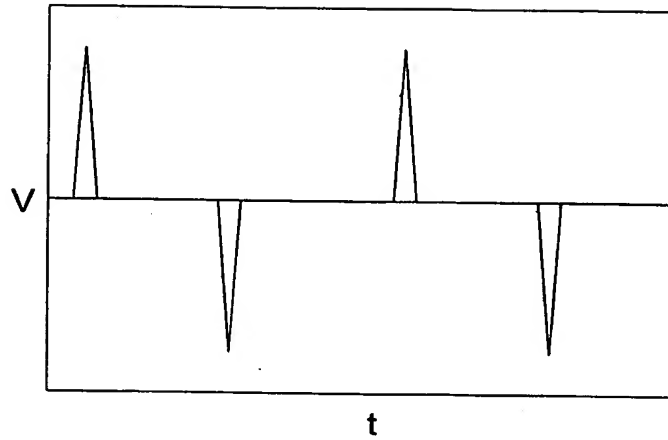


FIG. 2

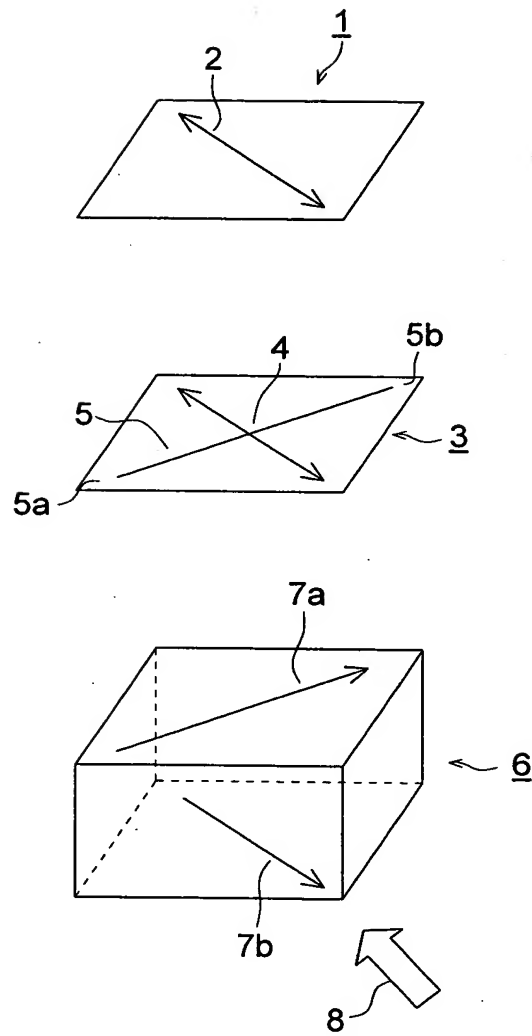


FIG. 3

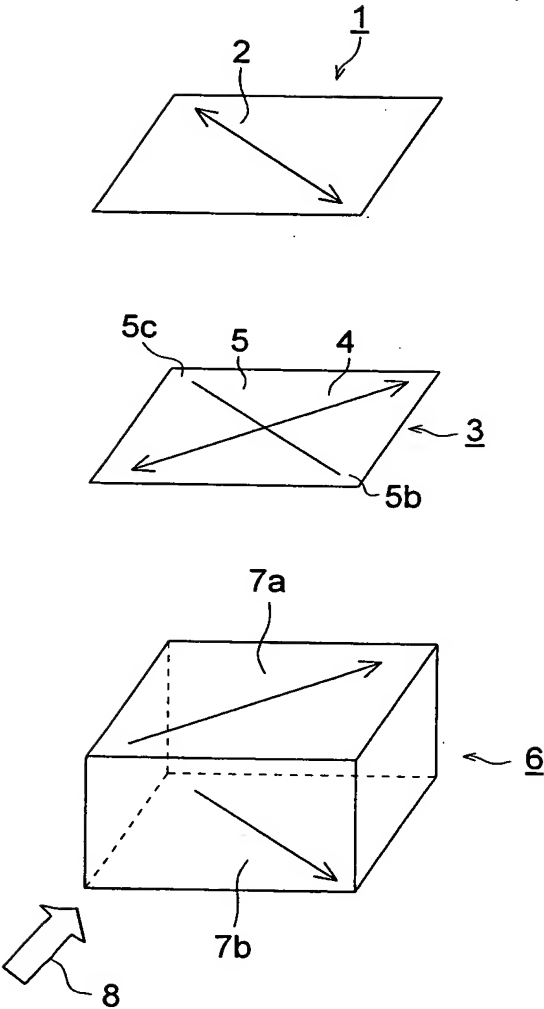


FIG. 4 (a)

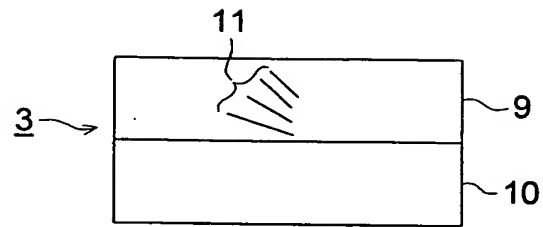


FIG. 4 (b)

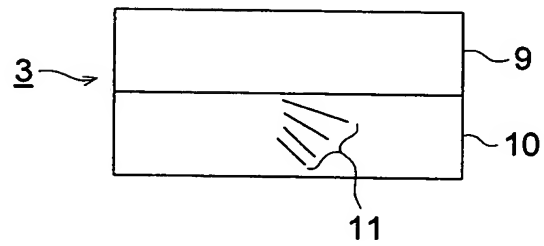


FIG. 5 (a)

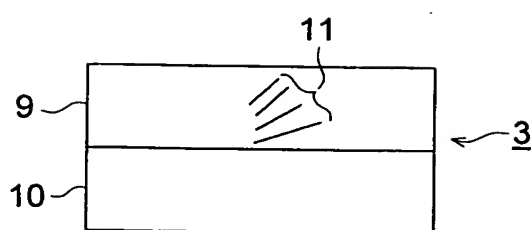
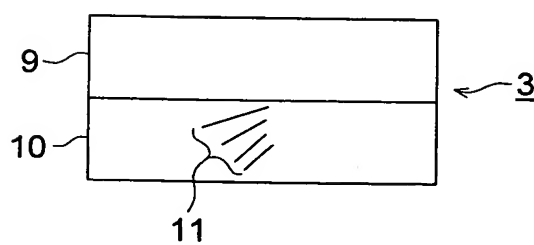


FIG. 5 (b)





[NAME OF DOCUMENT] ABSTRACT

[ABSTRACT]

[PROBLEM] To provide an optical compensation film which readily improves viewing angle characteristics of TN type LCD such as TN-TFT, and further to provide a polarized plate and a liquid crystal display apparatus with marked improvement of the viewing angle under a simple constitution, while employing said optical compensation film.

[SUMMARY] An optical compensation film comprising an optically biaxial cellulose ester film having thereon a layer, comprising a liquid crystalline compound, which is modified to an optically anisotropic layer upon fixing the orientation of said liquid crystalline compound.

[SELECTED DRAWINGS] None